SOME DISTRIBUTED PARAMETER OPTIMISATION PROBLEMS IN CHEMICAL ENGINEERING

by

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CONTENTS

Note Some of the material in Chapters 2 and 3 has already been published {50}.

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SUMMARY

For certain reaction schemes in which waste products are formed it is possible to selectively increase the output of the desired product from a tubular reactor of given length or a batch reactor of given volume by various programmes of distribution of one or more of the reactants. For a tubular reactor such distribution may take the form of addition of fresh reactant at a small number of fixed feed points along the reactor tube, the amount of feed being either equal for each feed point, or of such values that the output of desired product from the reactor is maximised. For a batch reactor there can be continuous feed of reactant and the rate of feed may be constant, or may be regulated in such a way as to optimise the performance of the reactor in some way.

This thesis is concerned with the problem of finding the optimal rate of addition policy for reactants to maximise the output of desired product from a given batch reactor. This is the sort of problem to which Pontryagin's Maximum Principle can be applied. A description of Pontryagin's principle and some of its simpler extensions is given, and a general criterion is developed from these which can be applied to reaction schemes to distinguish cases in which distributed addition of one or more of the reactants is advantageous.

For a particular system of parallel competitive reactions in which it is of advantage to distribute the addition of one of the reactants, the optimal addition-rate policy for this reactant is obtained for an isothermal batch reactor. Since this policy involves

instantaneous addition of reactant at the beginning and a rate of addition which tends to infinity towards the end of the batch time, the system is modified so that the rate of addition of reactant is bounded above, and the optimal addition-rate policy found for several values of this upper bound. A further modification to the system of specifying the total amount of reactant to be added is also made, and it is shown that, with this additional constraint applied, it is possible to remove the upper bound on the rate of addition. Further improvements in reactor performance may be obtained if the reaction temperature is optimised simultaneously with the rate of addition, and some preliminary investigations are made into such simultaneous control.

CHAPTER 1

INTRODUCTION

Many investigations into improving the performance of chemical reactors have been concerned with temperature control. It is perhaps natural that such control has been so well studied, as temperature is often the simplest and most obvious parameter through which a reaction rate may be influenced. Problems of temperature control which have arisen range from the simple problem of finding the optimal (constant) temperature in a single continuous stirred-tank reactor (C.S.T.R.), through the problem of finding the sequence of temperatures in a series of such reactors, to the problem of determining the optimal temperature profile in a tubular reactor, where the temperature profile is a function of a continuous variable, namely distance along the reactor.

For many of the latter two situations, the optimal control is a programme of decreasing temperature. It is well known {1 - 6} that, for a single reversible exothermic reaction in an ideal plug-flow tubular reactor, the optimal policy for a reactor of minimum volume for a given duty, or for maximum product for a given volume, is to maximise the reaction rate with respect to temperature at each point in the reactor. The optimal temperature control thus obtained is a profile of decreasing temperature along the reactor length. For more complicated reaction systems, the optimal policy is no longer that which maximises the reaction rate at each point in the reactor {7}. Nevertheless, the optimal control is again often a decreasing profile of temperature along the reactor. Bilous and Amundson {7}, for example, have shown that, for a sequential

reaction of the form

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad (1.1)$$

where B is the desired product, the optimal temperature profile is of a decreasing form. Further writers {8, 9}, however, have shown that this form of temperature control is optimal only when the activation energy of the second reaction is greater than that of the first. Further examples of optimal temperature profiles in reactors are summarised by Dyson et al {11}.

One means of obtaining a decreasing profile when a reaction is exothermic is by adding cold feed to the reaction mixture as the reaction proceeds. Such a means of control has been suggested {6, 10}, and Aris {12} has considered this form of control for a reaction system of several independent simultaneous irreversible reactions in a C.S.T.R. sequence, in which the feed to each reactor in the sequence consists of the output from the previous reactor mixed with cold unreacted feed from the inlet to the reactor sequence. By considering such a cascade of C.S.T.R.s with equal ~~volumes~~ holding-times, and letting the number in the cascade increase to infinity, their total volume being constant, a continuous model is obtained. This limiting model was used by Aris {12} to represent a batch reactor in which the temperature was controlled by regulating the addition of cold feed, and he showed how the optimal addition rate policy (a function of time) could be obtained for a single reversible exothermic reaction in such a reactor. Siebenthal and Aris {13} have studied in greater detail a similar problem of a batch reactor with delayed cold feed. Dyson and Horn {14} and Dyson and Graves {15} have looked at the problem of

maximising the exit concentration of a product from an ideal tubular reactor with distributed feed, in which the inlet feed to the reactor is preheated, and the temperature profile of the reactor is maintained by means of controlled distribution of cold feed along the length of the reactor (figure 1.1).

The addition of cold reactants as the reaction proceeds as a means of temperature control has the incidental effect of changing the composition of the reaction mixture at the point of addition of the cold feed, and, in certain circumstances, this change of composition may have a beneficial direct effect on the reactor performance, quite apart from its indirect effect through the temperature profile. Siebenthal and Aris {13} have given, as an example of a situation in which this beneficial effect can arise, the following reaction sequence

$$\begin{aligned} A + B &\rightleftharpoons C \\ C + D &\longrightarrow E \quad \text{(desired product)} \\ A + D &\longrightarrow F \quad \text{(waste product)} \end{aligned} \qquad (1.2)$$

where E is the desired product, and F is waste. Addition of D at the beginning of the reaction, when little of the intermediate C has yet been formed, causes reactant A to be consumed to form waste, so decreasing the amount of A which can ultimately be converted to product. In this case it is therefore of advantage to delay the addition of D to the reaction mixture. Denbigh {16} has mentioned that, in some organic nitration processes carried out in a cascade of C.S.T.R.s, it has been found that by making changes in the acid concentrations from one tank to the next, by means of supplementary feeds of acid to the C.S.T.R.s,

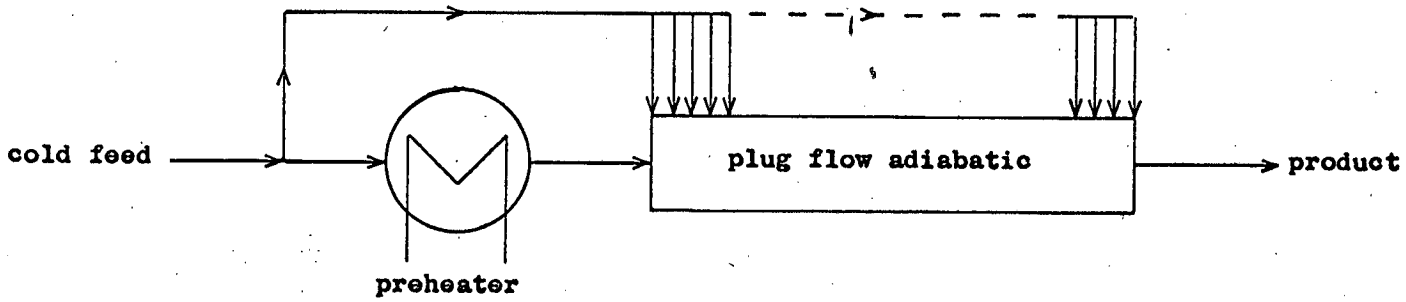


Figure 1.1

Cross-flow tubular reactor of the type considered by Dyson and Horn {14} and Dyson and Graves {15}, in which the optimal temperature profile is obtained by distribution of cold feed.

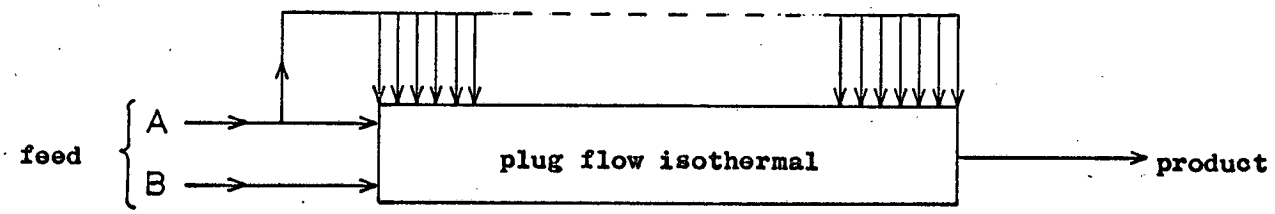


Figure 1.2

Isothermal cross-flow tubular reactor, in which the feed of one of the reactants is distributed.

significant improvements can be obtained. Denbigh has also shown {17} how improvements in the yield of the explosive cyclonite, formed by nitration of hexamethylene tetramine in a sequence of C.S.T.R.s, can be obtained by distributing the feed of the hexamethylene tetramine between different tanks in the sequence.

Kramers and Westerterp {18} have surveyed the yields of different types of reactors for a system of competing parallel reactions in isothermal conditions

$$\begin{aligned} A + B &\rightarrow C \quad \text{(product)} \\ A + A &\rightarrow D \quad \text{(waste)}. \end{aligned} \tag{1.3}$$

Yields were calculated for a C.S.T.R., plug-flow tubular reactor, and an idealised cross-flow reactor of the type shown in figure 1.2, in which the distributed feed of A is controlled so as to maintain a constant concentration of A along the reactor length. All reactors gave the same degree of conversion. The cross-flow reactor in this comparison gave a higher yield of product and had lower total volume than either the C.S.T.R. or the plug-flow tubular reactor.

van de Vusse and Voetter {19}, using the same reaction scheme as above (equations (1.3)), extended the ideal cross-flow reactor problem to that of finding an approximate optimal feed distribution profile for reactant A for maximum selectivity of product, and also for maximum yield of product, by the method of parametric expansion (see, for example, Storey {20}).

As Kramers and Westerterp {18} pointed out, in a practical cross-flow reactor the optimal distribution of reactant A for the

reaction scheme of equations (1.3) would be approximated by a few side-streams only. They cited as an example of such a reactor that studied by Messikommer {21}, who maximised the yields of such reactors with different numbers of feed points, with again the isothermal reaction scheme given by equations (1.3), by adjusting the amount of reactant A added at each feed point. It was found that the value of the reactor yield was relatively insensitive to the number of feed points and to the actual distribution of feed of reactant A, a feed of equal fractions to each feed point giving only a small decrease in yield.

Although an ideal continuous cross-flow reactor is unrealistic, its batch reactor analogue is not. For a batch reactor, the feed distribution profile becomes a function of time instead of distance along the reactor. The implementation of an optimal rate of addition control then becomes a realistic possibility.

An example of a semi-batch reactor system with a continuous feed of reactant is given in an organic chlorination reaction of the type

$$RH + Cl_2 \rightarrow RCl + HCl \qquad (1.4)$$

which is often carried out in a semi-batch reactor, where chlorine is bubbled through the liquid reactant at an essentially constant temperature until the required degree of conversion is obtained. By making a number of simplifying assumptions, Hawkins {22} has been able to derive a mathematical representation of such a reactor based on the observation that, for such a system, the reaction rate is low, and comparable with the rate of dissolution of chlorine. By application of the calculus of variations, he obtained an optimal addition rate policy for chlorine,

and showed that the batch time for a given conversion could be reduced significantly by using the optimal policy rather than the conventional policy of constant rate of addition of chlorine.

Although it has been recognised that, for certain isothermal reaction systems, improvements in reactor performance can be achieved by distribution of one of the reactants, such situations have received little attention. The continuous cross-flow reactor of Kramers and Westerterp {18} (figure 1.2) cannot be realised in practice, but as a model it gives an upper limit to what may be achieved in more practical arrangements. The batch reactor analogue, however, can be realised in practice, and although applying an optimal rate of addition may be difficult and the cost of implementing it may outweigh the advantages to be gained, it again serves as a standard of excellence. Further study of means of improving reactor performance by regulating the addition of reactants is needed, and as a first step it is logical to consider ideal reactors with continuous distribution of feed, as in the continuous cross-flow reactor shown in figure 2.1, and the batch reactor with delayed reactant addition.

The purpose of the present thesis is to investigate the optimal addition rate policy for such a batch reactor. As a first step a criterion is developed to distinguish cases in which addition of all the reactants at the beginning of the batch is non-optimal. Examples of the application of this criterion are given to simple reaction schemes, for which it is possible to deduce by general reasoning whether distributed addition of a reactant is advantageous. For an ideal reactor with one particular reaction scheme in which simultaneous initial addition is non-optimal for one of the reactants, the optimal addition-rate profile

is found, and this system is then progressively modified by applying various limitations on the rate of addition control. Finally the effect of simultaneously controlling the temperature of the reaction mixture is also considered.

The calculation methods and other deductions throughout the thesis, including those for the criterion mentioned above, are based on the Maximum Principle of Pontryagin and his co-workers {23, 24}. Before developing this criterion, therefore, an introduction to the maximum principle and its properties is given.

CHAPTER 2

PONTRYAGIN'S MAXIMUM PRINCIPLE AND ITS APPLICATION IN DEVELOPING A CRITERION FOR NON-OPTIMALITY OF SIMULTANEOUS ADDITION OF REACTANTS

2.1 Description of the Maximum Principle

The determination of an optimal rate of addition policy of a reactant to a batch reaction is the type of problem to which the maximum principle of Pontryagin et al {23, 24} is suited. The maximum principle is a branch of the calculus of variations, from which it can be derived {25}, and is quite closely related {24, 26, 27} to the dynamic programming algorithm of Bellman {28}. A good elementary account of the maximum principle can be found in the papers of Rozonoer {26}, while Katz {29} has given an introduction to the maximum principle in chemical engineering terms. Siebenthal and Aris {13, 30} have given some examples of the application of the maximum principle to some simple chemical engineering problems.

The maximum principle aims to solve the following problem. Given a set of first order ordinary differential equations (normally with respect to time) describing the behaviour of the system under consideration

$$\frac{dx_i}{dt} = f_i(x_1, x_2, \ldots x_n, u_1, u_2, \ldots u_m) \quad i = 1, 2, \ldots n \qquad (2.1)$$

(where x_i are the variables describing the state of the system, and u_j the variables by which the system may be directly controlled), together with specified initial conditions

$$x_i(0) = x_i^o \qquad i = 1, 2, \ldots n \qquad (2.2)$$

choose $u_j(t)$, $j = 1, \ldots m$, so that an objective function of the form

$$P = \sum_{i=1}^{n} \alpha_i x_i (\tau) \qquad (2.3)$$

is maximised (or minimised), where the α_i are constants, and τ represents the total time of operation of the system under consideration. This form of objective function may seem a little special, but more complicated forms of objective function can usually be reduced to this form by construction of additional variables.

n adjoint variables are introduced, satisfying the equations

$$\frac{d\lambda_i}{dt} = - \sum_{j=1}^{n} \lambda_j \frac{\partial f_j}{\partial x_i} \qquad i = 1, 2, \ldots n \qquad (2.4)$$

together with boundary values, specified at $t = \tau$

$$\lambda_i (\tau) = - \alpha_i \text{ for minimisation of the objective function} \qquad (2.5.a)$$

$$\lambda_i (\tau) = \alpha_i \text{ for maximisation of the objective function.} \qquad (2.5.b)$$

A Hamiltonian function can now be formed

$$H(\lambda, x, u) = \sum_{i=1}^{n} \lambda_i f_i (x, u). \qquad (2.6)$$

Pontryagin's maximum principle now states that, if $u_j(t)$, $j = 1, 2, \ldots m$, are optimal control functions, and equations (2.1) and (2.4), together with respective boundary conditions (2.2) and (2.5), are solved for these $u_j(t)$, then the $u_j(t)$ have the property that they maximise the Hamiltonian H in equation (2.6) at each t, where $x_i(t)$ and $\lambda_i(t)$ are considered constant for this maximisation. It must further be true that this maximum value of H is a constant, being zero if τ is also optimal.

There are several extensions {24} to the basic maximum principle

as it is stated above, but only those used later in this thesis will be given here:

(1) If the controls $u_j(t)$ are subject to simple constraints of the form

$$u_{min}^{(j)} < u(t) < u_{max}^{(j)} \qquad (2.7)$$

then the maximum principle remains as stated, the $u_j(t)$ being chosen from within their permitted range to maximise the Hamiltonian.

(2) If k of the final state variables are specified

$$x_i(\tau) = x_i^f \quad i = 1, 2, \ldots k < n \qquad (2.8)$$

then the boundary conditions on the adjoint variables become

$$\lambda_i(\tau) = \pm \alpha_i \quad i = k + 1, \ldots n \qquad (2.9)$$

where the positive sign is taken for a maximisation problem. The boundary values of the k adjoint variables corresponding to the state variables of which the terminal values are fixed, are unspecified.

The direct way of solving an optimisation problem by means of the maximum principle would be to simultaneously solve the differential equations for the state variables (equations (2.1)) and for the adjoint variables (equations (2.4)), obtaining the optimal control profiles by maximising the Hamiltonian (equation (2.6)) at each point. However the boundary values of the state variables (equation (2.2)) and of the adjoint variables (equation (2.5)) are given at opposite ends of the time interval of interest. This two point boundary value problem is not unique to the maximum principle; it appears in various guises in the classical treatment of the calculus of variations and in dynamic programming. In the

direct solution of the maximum principle it is therefore necessary to make guesses at the terminal values of one of the sets of variables at the opposite end of the time interval to which their boundary values are specified.

In the forwards method of solution, the initial values of the adjoint variables are estimated and the adjoint and state variable equations solved forward in time (with the controls u_j chosen so as to maximise the Hamiltonian at each point) to give final values $\lambda_i(\tau)$ for the adjoint variables, which will not in general be equal to the required terminal values. $\lambda_i(0)$ are then adjusted until the boundary values are satisfied. In the backwards solution, $x_i(\tau)$ are estimated, and the adjoint variable and state variable differential equations integrated backwards in time to obtain values of $x_i(0)$. Again, iteration on the guessed values of $x_i(\tau)$ will be required.

One of the obvious difficulties in applying these so called "boundary value iteration" methods is the problem of obtaining a suitable iteration scheme [32]. But in addition to this problem, more serious computational difficulties may arise as a consequence of the fact that one of the sets of state variable and adjoint variable differential equations is of necessity integrated in the "wrong" direction i.e. towards the point at which the boundary values are specified. It has been suggested by Rosenbrock and Storey [31] that when these equations are solved numerically in this fashion they may prove unstable. Latour [32] has more specifically suggested that, in the types of problems encountered in chemical engineering, the optimal solutions are of such a form that the adjoint variable equations are inherently unstable in whichever direction

they are integrated, and Aris {8} has similarly found that boundary value iteration methods of solution may lead to considerable computational difficulties due to instability of the adjoint variable differential equations.

Apart from such computational difficulties in obtaining the optimal control of a system by application of Pontryagin's maximum principle, there are mathematical difficulties of a more fundamental nature. It is well known {26} that Pontryagin's maximum principle is only a necessary condition for the maximisation (or minimisation) of the objective function of interest, and so the possibility exists of finding solutions which satisfy the maximum principle, but which do not maximise (or minimise) the objective function.

This difficulty has been discussed by Coward and Jackson {9}, who considered the problem of determining the optimal temperature profile for the system of successive reactions originally suggested by Bilous and Amundson {7} (see equation (1.1)). Problems of maximising and minimising the exit concentration of the intermediate B for different relative activation energies of the two reactions were investigated, and Coward and Jackson {9} showed that, although a number of temperature profiles could be found which satisfied the maximum principle, only one of these was usually optimal. In the examples chosen, the reaction system was sufficiently simple that the form of the solutions which satisfied the maximum principle could be deduced largely by general reasoning, and those which were not optimal profiles could mostly be identified without difficulty.

A similar situation of several control profiles satisfying the

maximum principle in a more complicated problem has been discussed by Siebenthal and Aris {30}. In this latter case, the general forms of the solutions could be deduced by general reasoning, but to determine which was the true optimal control it was necessary to numerically evaluate the objective function for each.

It is clear that applying Pontryagin's maximum principle to determine optimal control profiles is not simply a matter of generating and solving the necessary state variable and adjoint variable equations and maximising a Hamiltonian function. Even if there are no computational difficulties of the types already mentioned {8, 31, 32}, such blind numerical attack is unlikely to succeed if multiple solutions satisfying the maximum principle, as encountered by Coward and Jackson {9} and by Siebenthal and Aris {30}, are liable to occur. It has been pointed out by Latour {32} that, because of the possibilities of these sorts of difficulties, the maximum principle cannot yet be regarded as a routine tool of the chemical engineer, and considerably more experience of its employment must be obtained before its full usefulness can be exploited. For this reason, the investigation of the proposed problem of distributed reactant addition will be investigated by means of Pontryagin's maximum principle, and it will be shown that, while difficulties can occur which would ensure the failure of a direct numerical attack, these can be overcome by deductions from the properties of the system and from Pontryagin's condition.

As an example of the employment of the maximum principle in a chemical engineering problem, and as a preliminary to finding an optimal rate of addition policy for a reaction system, the optimality of the

simultaneous addition of reactants to a batch reaction at the beginning of the batch time will be investigated.

2.2 The Optimality of Simultaneous Addition of Reactants at the Beginning of a Reaction

The equivalence of the tubular cross-flow reactor and the batch reactor with continuous feed has already been discussed. Since the batch reactor form is more realistic, this model will be used in the investigations in the following chapters. However the results obtained will normally be directly applicable to cross-flow tubular reactors of the type shown in figure 1.2 by substituting distance along the tubular reactor for time since the beginning of the batch.

An example of a reaction scheme has already been given (equation 1.3) in which it was deduced that distributing the addition of a reactant to a batch reactor is likely to increase the final concentration of the product. For other simple reaction schemes, similar reasoning can give some insight into the usefulness of distributing the addition of a reactant, but if the kinetics are more complicated such deductions may not always be possible. It would be helpful to have some means of distinguishing cases where distributed reactant addition will give improvement in reactor performance, which could be applied to all reaction systems whose kinetics can be written down.

Consider an isothermal batch reactor. The substances reacting together in this reactor can be divided into reactants, which are present initially in or are added to the reactor, and products, which are present

as a result of chemical reaction. If the substances in the reactor are numbered from 1 to n, then the subset of these numbers which represent reactants will be denoted by I. If the number of moles of the i'th substance present in the reactor is c_i, then the c_i satisfy the following equations and boundary conditions

$$\frac{dc_i}{dt} = r_i(t) + \sum_{r=1}^{R} \nu_i^r \rho^r(c); \quad c_i(0) = 0 \quad (i \in I) \tag{2.10.a}$$

$$\frac{dc_i}{dt} = \sum_{r=1}^{R} \nu_i^r \rho^r(c) \quad ; \quad c_i(0) = 0 \quad (i \notin I) \tag{2.10.b}$$

where $r_i(t)$ is the rate of addition of the i'th reactant to the reactor, ν_i^r is the stoichiometric coefficient of the i'th reactant in the r'th independent chemical reaction, ($r = 1, 2, \ldots R$), and $\rho^r(c)$ is the rate of the r'th reaction, a function of the number of moles of each of the chemical substances in the reaction.

If $q_i(t)$ is the total amount of reactant i added during the interval $0 \to t$, then

$$\frac{dq_i}{dt} = r_i(t); \quad q_i(0) = 0; \quad q_i(\tau) = Q_i \quad (i \in I) \tag{2.11}$$

where Q_i is the total amount of reactant i to be added during the total batch time $0 \to \tau$.

The object is to choose the rates of addition $r_i(t)$ during the batch time $0 \leqslant t \leqslant \tau$ so that an objective function of the form

$$P = \sum_{i \notin I} \alpha_i c_i(\tau) \tag{2.12}$$

is maximised.

This problem as stated is of the type to which the maximum principle can be applied. Equations (2.10) are equivalent to equations (2.1) and boundary conditions (2.2), while equations (2.11), which have additional boundary values at $t = \tau$ are equivalent to equations (2.8). The objective function, equation (2.12), is of the same form as equation (2.3).

The rates of addition of the reactants are bounded below by the physical condition that they may not be negative, and they will normally also be bounded above

$$0 \leq r_i(t) \leq r_{i\,max}. \tag{2.13}$$

Adjoint variables λ_i and μ_i corresponding to c_i and q_i are introduced

$$\frac{d\lambda_i}{dt} = -\sum_{r=1}^{R} \frac{\partial \rho^r(c)}{\partial c_i} \sum_{j=1}^{n} \lambda_j \nu_j^r \quad (i = 1, 2, \ldots n) \tag{2.14}$$

and

$$\frac{d\mu_i}{dt} = 0 \qquad (i \in I) \tag{2.15}$$

together with boundary conditions

$$\lambda_i(\tau) = 0 \qquad (i \in I) \tag{2.16.a}$$

and

$$\lambda_i(\tau) = \alpha_i \qquad (i \notin I). \tag{2.16.b}$$

As the $q_i(\tau)$ are specified (equation (2.11)), the corresponding adjoint variables μ_i have no specified boundary conditions at $t = \tau$.

A Hamiltonian function, defined by equation (2.6), can now be constructed

$$H = \sum_{i \in I} (\lambda_i + \mu_i) r_i + \sum_{r=1}^{R} \rho^r(c) \sum_{i=1}^{n} \lambda_i \nu_i^r . \qquad (2.17)$$

If P is to be maximised, $r_i(t)$ must be chosen so that H is maximised with respect to the $r_i(t)$ at each t, and this value of H_{max} obtained must be constant throughout $0 \leqslant t \leqslant \tau$.

Consider the addition rate policy

$$\left.\begin{aligned} r_i &= r_{i\,max} && 0 \leqslant t < \frac{Q_i}{r_{i\,max}} \\ r_i &= 0 && \frac{Q_i}{r_{i\,max}} < t \leqslant \tau \end{aligned}\right\} \quad \text{all } i \in I \qquad (2.18)$$

where a quantity Q_i of each reactant is added at its maximum rate at the beginning of the batch time.

The Hamiltonian is linear in the rates of addition, the coefficients of the r_i being $(\lambda_i + \mu_i)$. If the proposed addition rate policy is to maximise the Hamiltonian, then

$$\left.\begin{aligned} &\lambda_i + \mu_i \geqslant 0 \text{ for } 0 \leqslant t < \frac{Q_i}{r_{i\,max}} \\ &\lambda_i + \mu_i \leqslant 0 \text{ for } \frac{Q_i}{r_{i\,max}} < t \leqslant \tau \end{aligned}\right\} \quad \text{all } i \in I. \qquad (2.19)$$

It follows from equation (2.15) that the μ_i are constant. $\mu_i(\tau)$ is unspecified, and since the other adjoint variables are not affected by the values of the μ_i, these latter are free to be chosen. In particular they may take the values

$$\mu_i(t) = -\lambda_i \left(\frac{Q_i}{r_{i\,max}}\right). \qquad (i \in I) \qquad (2.20)$$

Then $(\lambda_i + \mu_i) = 0$ at $t = \dfrac{Q_i}{r_{i\,max}}$, and it follows that equations (2.19)

can be satisfied if and only if

$$\left.\begin{aligned} \lambda_i(t) \geqslant \lambda_i\left(\frac{Q_i}{r_{i\,max}}\right) \quad \text{for all } t < \frac{Q_i}{r_{i\,max}} \\ \lambda_i(t) \leqslant \lambda_i\left(\frac{Q_i}{r_{i\,max}}\right) \quad \text{for all } t > \frac{Q_i}{r_{i\,max}} \end{aligned}\right\} \text{all } i \in I. \quad (2.21)$$

Now let $r_{i\,max} \to \infty$, so that $\frac{Q_i}{r_{i\,max}} \to 0$. Then the first inequality of (2.21) loses significance, and the second reduces to

$$\lambda_i(t) \leqslant \lambda_i(0) \quad \text{for all } t > 0 \quad (i \in I). \quad (2.22)$$

This is the necessary condition that simultaneous addition of all the reactants at the beginning of the batch should be optimal. When this test fails for one or more adjoint variables, simultaneous initial addition is non optimal, and when this occurs for only one adjoint variable, the reactant corresponding to that adjoint variable can have its addition distributed to advantage.

To test the optimality of the simultaneous addition policy for any given reaction system, equations (2.10.a) and (2.10.b) are integrated numerically forward in time from $t = 0$ to $t = \tau$, with the boundary conditions for equation (2.10.a) replaced by $c_i(0) = Q_i$. The equations (2.14) for the adjoint variables are then integrated backwards in time, using the concentration profiles already calculated. The points at which the adjoint variables corresponding to the reactants take their largest values are noted, and if any of these maxima occur other than at $t = 0$, then the addition of all the reactants at the beginning of the batch is non-optimal.

Jackson {33} has derived results identical to the above as a

special case of a more general variational result in which the performance of a reactor of general flow structure is related to small changes in this structure. The above derivation shows that the same results can be obtained from the maximum principle.

The criterion can now be tested by applying it to some reaction systems where the optimality of simultaneous addition can be deduced by physical reasoning. For example, consider the following reaction systems

$$A + B \xrightarrow{k_1} C \qquad (2.23)$$

and

$$\left.\begin{array}{l} A + B \xrightarrow{k_1} C \\ A + 2B \xrightarrow{k_2} D \end{array}\right\} \text{ with desired product C} \qquad (2.24)$$

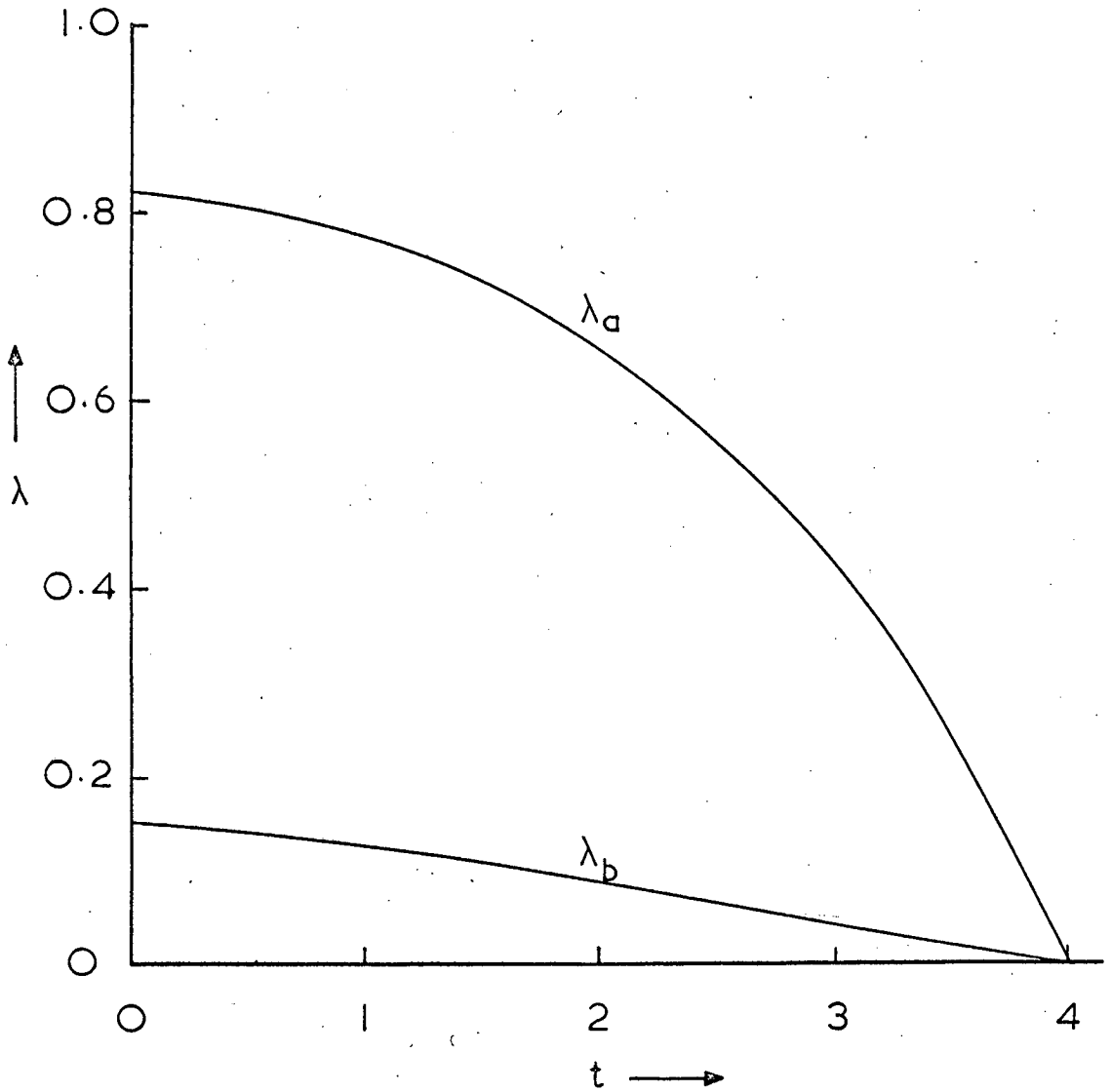
where it is assumed that the reaction kinetics are in accordance with the stoichiometry of the equations: in (2.24), the reaction to waste D is first order with respect to A and second order with respect to B, while all other reactions are first order with respect to A and to B. The reactions are irreversible.

It is clear that delaying the addition of either reactant in (2.23) would be detrimental to the production of C. However, in the reaction set (2.24), originally suggested by Denbigh {34}, high concentration of B favours the undesired reaction, because of the higher order of B in this reaction, and so an increase in the amount of product C formed would be expected from adding B slowly to the reaction mixture so that the concentration of B is kept low.

The equations for the concentrations of the reactants and for the corresponding adjoint variables were integrated numerically, as

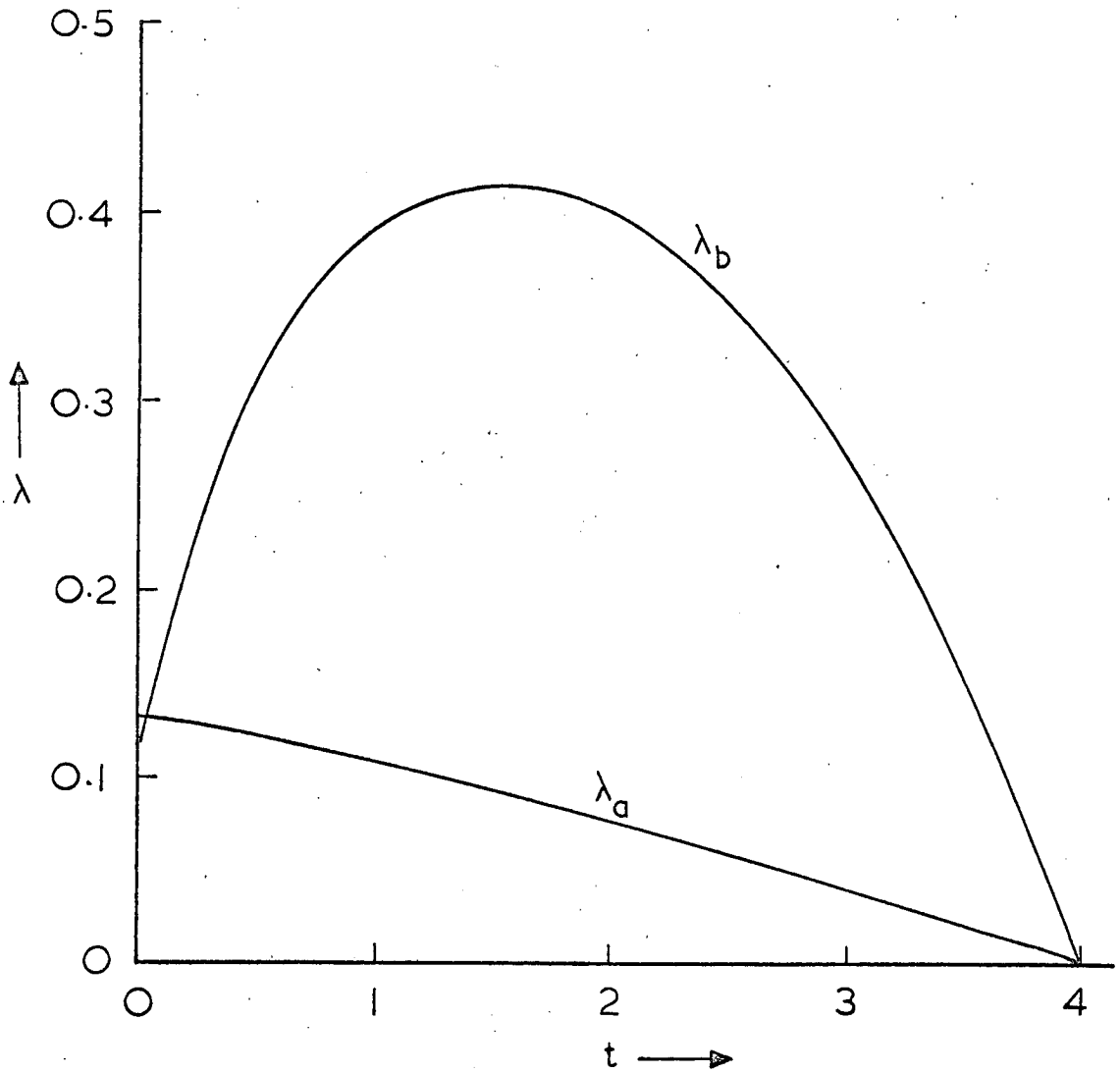
previously outlined, for a range of values of initial concentrations, kinetic rate constants, and batch times. As expected, for (2.23) the adjoint variables corresponding to reactants A and B are monotonic decreasing in time (Graph 2.1), so satisfying the necessary conditions for optimality of simultaneous addition. For system (2.24), however, while the adjoint variable λ_a corresponding to reactant A always takes its maximum value at $t = 0$ for different sets of reaction parameters, $\lambda_b(0)$ does not represent the maximum value of $\lambda_b(t)$ for any values of reaction parameters (Graph 2.2). The necessary condition is therefore not satisfied for reactant B, which infers that improvements in the final concentration of product would result from distributing the addition of B throughout the batch. This is in line with Denbigh's arguments {34}. Graphs (2.1) and (2.2) represent graphs of λ_a and λ_b vs. time for reaction systems (2.23) and (2.24) respectively for typical sets of reaction parameters.

The mathematical criterion is of real value for systems of more complicated kinetics, when it is not easy to argue on physical grounds whether distributed addition of a reactant will prove beneficial. However a degree of caution is sometimes required in interpreting the results. For example, for the system suggested by Siebenthal and Aris {13} (equation 1.2), it was suggested that reactant D should not all be added at the beginning of the reaction. Application of the mathematical criterion indicates that reactant D should not all be added to the batch at the beginning, as expected, but it also shows that, for certain combinations of reaction parameters, λ_a, corresponding to reactant A, also does not take its maximum value at $t = 0$, suggesting that perhaps reactant



Graph 2.1

Adjoint variables for the reaction $A + B \xrightarrow{k_1} C$ after simultaneous addition of the reactants. $a_o = 1$, $b_o = 1.5$, $k_1 = 1$, and batch time $\tau = 1$.



Graph 2.2

Adjoint variables for the reaction pair $A + B \xrightarrow{k_1} C$, $A + 2B \xrightarrow{k_2} D$, after simultaneous addition of reactants. $a_o = 1$, $b_o = 1$, $k_1 = 1$, $k_2 = 2$, and batch time $\tau = 4$.

A should also have its addition distributed. This occurs when the reversible reaction to intermediate C is not strongly favoured towards the forward reaction, and when the kinetic rate constant of the reaction to waste product F is not small compared with the rate constants for the other reactions.

The explanation appears to be that, if the initial concentration of A as well as that of D is high, the reaction to waste proceeds so rapidly that, not only is the amount of D which is left to react with intermediate C reduced, but the amount of A which can produce C is also greatly reduced. In circumstances of high initial concentration of D, therefore, it would appear that it is of advantage to reduce the initial concentration of A by distributing its addition, so as to reduce the rate of the reaction to waste. It is probable that, once an optimal addition policy for D was implemented, the concentration of D would be maintained at a sufficiently low level that the waste reaction would proceed at a low rate and the above effects would not occur. It then seems more likely that a high initial concentration of A, obtained by simultaneous addition of A, would be required at the beginning of the reaction, since the concentration of the intermediate C could then build up quickly and the rate of formation of the product E could be kept as high as possible.

This example is a relatively simple one, in which it is possible to partly explain the results obtained from the mathematical test. It appears that when the addition of two or more of the reactants at the beginning of the reaction is non-optimal, the addition of one (or more) of these reactants at the beginning may no longer be non-optimal when the additions of the others of these reactants are distributed. It should be

emphasised that the criterion only locates cases in which simultaneous initial addition is non-optimal. It does not pretend to say just which reactants should be distributed, unless only one of the adjoint variables does not take its maximum value at $t = 0$. Therefore, in more complicated reactions, the results of this test should be interpreted with caution if simultaneous addition at the beginning of the batch appears to be non-optimal for more than one reactant, particularly when this situation occurs for only certain combinations of reaction parameters.

CHAPTER 3

THE OPTIMAL DISTRIBUTED ADDITION FOR AN ISOTHERMAL BATCH REACTION

It has been suggested by Denbigh {34} that for the reaction scheme

$$\begin{aligned} A + B &\xrightarrow{k_1} C \quad \text{(product)} \\ A + 2B &\xrightarrow{k_2} D \quad \text{(waste)} \end{aligned} \tag{3.1}$$

in an isothermal batch reactor, the final concentration of C can be increased by adding B slowly to the batch so that the concentration of B is always kept low. It was shown in Chapter 2 that simultaneous addition of the reactants for reaction scheme (3.1) at the beginning is non-optimal for reactant B (Graph 2.2).

This reaction scheme is sufficiently simple that some of the features of the optimal control can be reasoned on physical grounds, and is therefore suitable for further investigation to discover the precise form of the optimal addition rate profile.

3.1 No Constraint on the Maximum Rate of Addition

In this case it is possible to obtain analytically a trajectory which satisfies the maximum principle. The control profile can in this case be obtained in two ways: by considering the rate of addition of reactant as the control variable; and by considering that the concentration of B can be directly controlled. These two approaches will be examined in turn.

3.1.1 Rate of addition as the control variable

The differential equations for the system are

$$\frac{da}{dt} = -k_1 ab - k_2 ab^2 \tag{3.2}$$

$$\frac{db}{dt} = -k_1 ab - 2k_2 ab^2 + r \tag{3.3}$$

$$\frac{dc}{dt} = k_1 ab \tag{3.4}$$

where a, b, c, s represent the concentrations of A, B, C, D respectively, k_1 and k_2 are the reaction rate factors for the reaction to form product C and the reaction to form waste D respectively, and $r = r(t)$ is the rate of addition of B, which is a function of time t. The reactions are irreversible and the batch reactor is isothermal. It is assumed in writing down the above equations that the addition of substance B has no direct influence on the concentrations of the other substances in the reactor by a dilution effect. This is not generally true, but is approached in the situation of reactions taking place in a dilute solution of an inert solvent. Attention will be limited to such systems for algebraic simplicity; there is no difficulty in principle in extending the theory to cover less idealised models.

The boundary conditions on these concentrations are

$$a(0) = a_o; \quad b(0) = c(0) = 0 . \tag{3.5}$$

The objective function to be maximised is

$$P = c(\tau) . \tag{3.6}$$

Adjoint variables corresponding to $a \rightarrow c$ are formed

$$\frac{d\lambda_a}{dt} = k_1 b(\lambda_a + \lambda_b - \lambda_c) + k_2 b^2(\lambda_a + 2\lambda_b) \qquad (3.7)$$

$$\frac{d\lambda_b}{dt} = k_1 a(\lambda_a + \lambda_b - \lambda_c) + 2k_2 ab(\lambda_a + 2\lambda_b) \qquad (3.8)$$

$$\frac{d\lambda_c}{dt} = 0 \qquad (3.9)$$

with boundary conditions

$$\lambda_c(\tau) = 1; \quad \lambda_a(\tau) = \lambda_b(\tau) = 0 . \qquad (3.10)$$

It follows immediately from equations (3.9) and (3.10) that

$$\lambda_c(t) = 1 . \qquad (3.11)$$

The Hamiltonian function is then

$$H = \lambda_b r - k_1 ab(\lambda_a + \lambda_b - 1) - k_2 ab^2(\lambda_a + 2\lambda_b) \qquad (3.12)$$

where the value of λ_c has been replaced according to equation (3.11).

At present, no bound is to be imposed on the total amount of B added, nor on the maximum rate of addition of B. H is linear in r, and is therefore maximised by

$$\begin{aligned} r &\to \infty \quad \text{for} \quad \lambda_b > 0 \\ r &= 0 \quad \text{for} \quad \lambda_b < 0 . \end{aligned} \qquad (3.13)$$

r may take intermediate values for a finite time interval only when $\lambda_b = 0$ for the duration of this interval. Such a segment, if it exists, will be called a "singular segment". Segments of $r = \infty$, if they exist, can make physical sense only if their durations are zero, when they correspond to instantaneous additions of finite quantities of B at specific points in time. The optimal trajectory must therefore consist of segments of $r = 0$,

singular segments, and instantaneous additions of finite quantities of B, joined together in such a way that Pontryagin's condition is satisfied throughout the interval $0 \rightarrow \tau$.

For a singular segment, λ_b must vanish for the duration of the segment, and $\frac{d\lambda_b}{dt}$ must therefore also vanish. Equations (3.7) and (3.8) then reduce to

$$\frac{d\lambda_a}{dt} = k_1 b(\lambda_a - 1) + k_2 b^2 \lambda_a \tag{3.14}$$

$$0 = k_1 a(\lambda_a - 1) + 2k_2 ab\lambda_a . \tag{3.15}$$

Equation (3.15) can be rearranged to give

$$\lambda_a = \frac{k_1}{k_1 + 2k_2 b} . \tag{3.16}$$

Differentiating this with respect to time, and comparing the result with equation (3.14) eventually leads to

$$r = b(k_1 + 2k_2 b)(a + \frac{b}{2}) \tag{3.17}$$

which gives the rate of addition of B as a function of the concentrations of A and B. If this is now substituted into equation (3.3), the result is

$$\frac{db}{dt} = \frac{b^2}{2} (k_1 + 2k_2 b) \tag{3.18}$$

which, since it involves only b and t, can be integrated to give an equation for b as a function of time on the singular segment:

$$\frac{2k_2}{k_1} \ln \left(\frac{k_1 + 2k_2 b}{k_1 b}\right) - \frac{1}{b} = \frac{k_1 t}{2} + z \tag{3.19}$$

where z is the constant of integration.

Although it is difficult to justify at this stage, the values

of a and b at $t = \tau$ must be 0 and ∞ respectively. These terminal conditions are confirmed in later arguments in the alternative approach to the solution of this problem. Substitution of the condition $b \to \infty$ at $t \to \tau$ into equation (3.19) allows the constant of integration, z, to be evaluated, and the equation then simplifies to

$$\frac{2k_2}{k_1} \ln \left(\frac{k_1 + 2k_2 b}{2k_2 b} \right) - \frac{1}{b} = \frac{k_1}{2} (t - \tau) \qquad (3.20)$$

an equation relating b and t on the singular segment.

Substitution of $t = 0$ into this equation gives a positive non-zero value for b. Since in the reaction system, $b(0) = 0$ (equation (3.5)), an instantaneous addition of sufficient quantity of B to satisfy equation (3.20) is required to initiate the singular segment.

The value of a corresponding to a given value of b on the singular segment can be found if use is made of the constancy of the Hamiltonian when the maximum principle is satisfied. If the expression for λ_a (equation (3.16)) is substituted into (3.12), and λ_b is set to zero in this equation, an expression for H on the singular segment is obtained:

$$H = \frac{k_1 k_2 a b^2}{k_1 + 2k_2 b}. \qquad (3.21)$$

At $t = 0$, $a = a_o$, and b can be found on the singular segment from equation (3.20). By substituting these values of a and b into equation (3.21), the value of H can be calculated. Since H is constant along the singular segment, equation (3.21) represents the singular segment in the a - b plane, from which the value of a on the singular segment corresponding to

a given value of b can be found. It is therefore possible, by means of equations (3.20) and (3.21) to obtain profiles of a and b as functions of time along the singular segment.

A rate of addition policy which satisfies the maximum principle for this problem therefore consists of an instantaneous addition of a finite quantity of B at $t = 0$ to give an initial concentration of B, followed by a singular segment from $t = 0$ to $t = \tau$, on which the rate of addition r is given by equation (3.17). Profiles of a and b can be obtained in the manner outlined above, and the value of $c(\tau)$ can then be obtained from these a- and b-profiles by integration.

3.1.2 Concentration of reactant as control variable

By considering the concentration of reactant B as the control variable instead of the rate of addition of B, the application of the maximum principle leads to the same equations but without a singular segment condition.

If the extent of the first reaction of (3.1) at a time t is denoted by ξ_1, and that of the second reaction by ξ_2, then

$$\frac{d\xi_1}{dt} = k_1 b(a_o - \xi_1 - \xi_2); \quad \xi_1(0) = 0 \tag{3.22}$$

$$\frac{d\xi_2}{dt} = k_2 b^2(a_o - \xi_1 - \xi_2); \quad \xi_2(0) = 0 \tag{3.23}$$

where a_o is the initial concentration of A, and b, the concentration of B, is directly controllable. The adjoint variables satisfy the equations

$$\frac{d\eta_1}{dt} = \eta_1 k_1 b + \eta_2 k_2 b^2 \tag{3.24}$$

$$\frac{d\eta_2}{dt} = \eta_1 k_1 b + \eta_2 k_2 b^2 \tag{3.25}$$

and the objective function is given by

$$P = \xi_1 . \tag{3.26}$$

The boundary conditions of the adjoint variables are therefore

$$\eta_1(\tau) = 1; \quad \eta_2(\tau) = 0 . \tag{3.27}$$

The Hamiltonian can now be written:

$$H = (\eta_1 k_1 b + \eta_2 k_2 b^2)(a_o - \xi_1 - \xi_2) . \tag{3.28}$$

From equations (3.24) and (3.25)

$$\frac{d}{dt}(\eta_1 - \eta_2) = 0 \tag{3.29}$$

and it therefore follows from equations (3.27) and (3.29) that

$$\eta_1 = 1 + \eta_2 . \tag{3.30}$$

A weaker condition of the maximum principle is that the Hamiltonian should have a stationary value with respect to the control variable at each point in time, and if this gives a value of the control variable outside its permitted range, the nearer limiting value is taken. This condition must be used with care, as it gives no guarantee that the Hamiltonian is maximised. Using this weaker condition:

$$\frac{\partial H}{\partial b} = (\eta_1 k_1 + 2\eta_2 k_2 b)(a_o - \xi_1 - \xi_2) = 0 . \tag{3.31}$$

This must remain zero for the duration of the batch time, and therefore

the differential of equation (3.31) with respect to time must also be zero:

$$\frac{d}{dt}\left(\frac{\partial H}{\partial b}\right)_{\frac{\partial H}{\partial b}=0} \propto k_1 \frac{d\eta_1}{dt} + 2k_2 b \frac{d\eta_2}{dt} + 2k_2\eta_2\frac{db}{dt} = 0 \qquad (3.32)$$

which reduces to

$$\frac{db}{dt} = \frac{b^2}{2}(k_1 + 2k_2 b) \qquad (3.33)$$

which is identical to equation (3.18). The rest of the argument follows exactly as before.

On this occasion the boundary condition for equation (3.33)/(3.18) can be deduced. At $t = \tau$, the Hamiltonian (3.28) reduces to

$$H_\tau = k_1 b\,(a_o - \xi_1 - \xi_2)$$

which is obviously maximised by making b as large as possible. It follows from equation (3.2) that, if $b \to \infty$ at $t \to \tau$, a must $\to 0$. These provide the boundary conditions at $t = \tau$ assumed earlier in evaluating the constant of integration in equation (3.19).

It is now only necessary to show that the Hamiltonian of equation (3.28) has a stationary maximum. Substitution of equation (3.30) into equation (3.25) gives

$$\frac{d\eta_2}{dt} = k_1 b + \eta_2\,(k_1 b + k_2 b^2) \qquad (3.34)$$

with boundary condition $\eta_2 = 0$ at $t = \tau$ (equation (3.27)). It is clear that η_2 can never be positive, for if, at any time, η_2 were positive, it would continue to increase according to equation (3.34) (since b is always positive), and it would then not be possible to achieve the desired boundary value. It must also be true that η_2 must ~~also~~ be greater than

-1, for

$$\frac{d\eta_2}{dt} \leq -k_2 b^2 < 0 \text{ for } \eta_2 \leq -1 \qquad (3.35)$$

in which case η_2 would continue to decrease, when the boundary condition again could not be satisfied.

Thus, in $0 \leq t \leq \tau$

$$-1 < \eta_2 \leq 0; \quad 0 < \eta_1 \leq 1 \qquad (3.36)$$

The Hamiltonian is therefore of the form

$$H = \beta b - \gamma b^2 \qquad \beta, \gamma > 0$$

and thus always shows a positive maximum value. The use of the weaker condition of a stationary Hamiltonian is therefore satisfactory in this case.

This form of the example, where the concentration of B is considered directly controllable, is interesting in that it leads to the same control profile but without a singular segment. The fact that this approach leads to the same results as those obtained by the more realistic control of the rate of addition of reactant is a useful confirmation, which is nevertheless fortuitous in that the control variables in the two approaches are not equivalent. While the rate of addition, r, is bounded below by the physical condition that it may not be negative, no similar constraint was applied to the concentration of B when this was considered the control variable. Had the lower limit of r been demanded in the control profile when r was the control variable, the trajectory obtained by considering the concentration of B as directly controllable would have certainly been different.

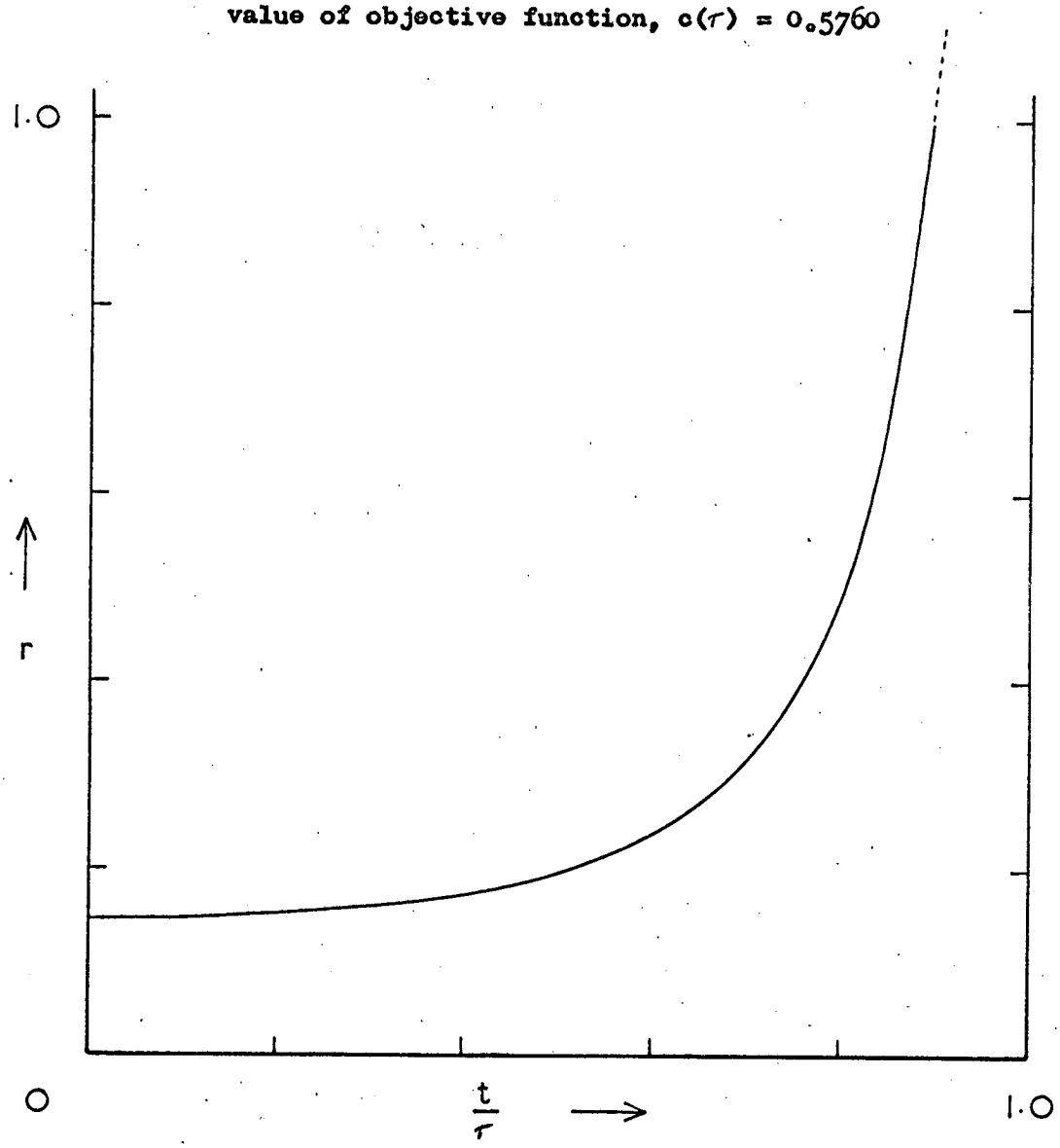
$a_o = 1$

$k_1 = 1$

$k_2 = 2$

$\tau = 4$

value of objective function, $c(\tau) = 0.5760$



Graph 3.1

control policy for r unconstrained

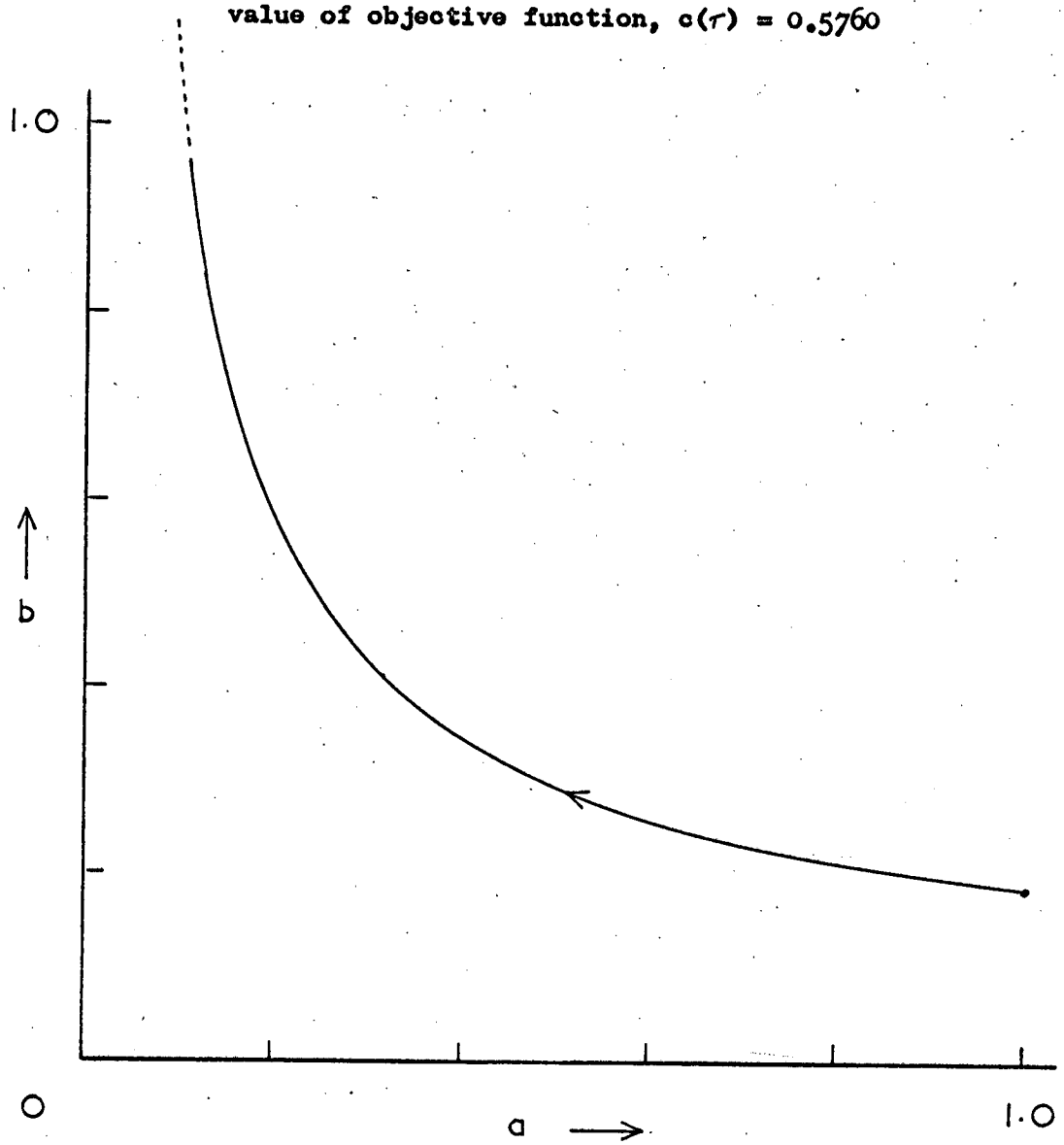
$a_o = 1$

$k_1 = 1$

$k_2 = 2$

$\tau = 4$

value of objective function, $c(\tau) = 0.5760$



Graph 3.2

solution trajectory in the a-b plane for the control policy of Graph 3.1

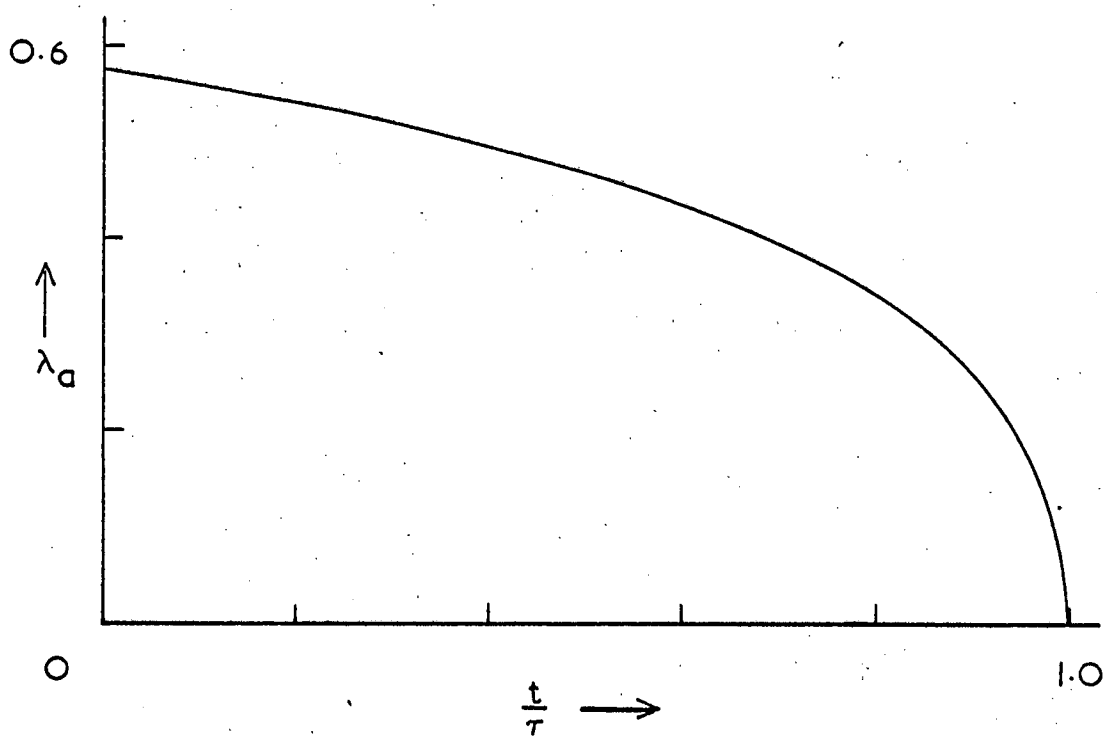
$a_o = 1$

$k_1 = 1$

$k_2 = 2$

$\tau = 4$

value of objective function, $c(\tau) = 0.5760$



Graph 3.3

adjoint variable λ_a for the control profile of Graph 3.1.

$\lambda_b = 0$ for $0 \leq t \leq \tau$.

Calculations of the control profile satisfying the maximum principle were made in the manner already described, and graphs plotted of the rate of addition vs. time (Graph 3.1), the a - b phase plane (Graph 3.2) and of the adjoint variable λ_a (Graph 3.3); λ_b is, of course, always zero.

As $b \to \infty$ at $t \to \tau$, the rate of addition of B (equation (3.17)) must similarly $\to \infty$. While instantaneous addition of a finite quantity of B at $t = 0$ is physically possible, it would not be possible in a practical reactor to arrange large rates of addition of B for finite time intervals, as required by the control policy, towards the end of the batch time. The system will therefore be investigated further with the modification of an upper limit on the rate of addition of B.

3.2 Constrained Rate of Addition

An upper limit of r_{max} will now be imposed on the rate of addition of B, so that a profile of r must be found which satisfies the maximum principle and on which r is chosen so that

$$0 \leqslant r \leqslant r_{max}.$$

For this modification to the original problem, the state variable and adjoint variable differential equations (equations (3.2) → (3.4), (3.7) → (3.9) respectively) and their boundary conditions (equations (3.5), (3.10)) are unaltered, and the Hamiltonian is given by equation (3.12)

$$H = \lambda_b r - k_1 ab\ (\lambda_a + \lambda_b - 1) - k_2 ab^2\ (\lambda_a + 2\lambda_b).$$

Since H is linear in r, it is maximised by

$$\begin{aligned} r &= r_{max} \quad \text{for } \lambda_b > 0 \\ r &= 0 \quad\ \ \text{for } \lambda_b < 0 \end{aligned} \tag{3.37}$$

and r may take values intermediate between its limits only on a singular segment, for which $\lambda_b = 0$. The required control profile will consist of segments of $r = 0$, $r = r_{max}$, and of singular segments, joined together in such a way that the maximum principle is satisfied throughout the interval $0 \leq t \leq \tau$. The present task is to deduce in what way these sections of the final profile are joined.

3.2.1 Exact solution

At $t = \tau$, by substitution of the boundary conditions (equation (3.10)) ~~end of equation (3.11)~~, equation (3.8) reduces to

$$\frac{d\lambda_b}{dt} = - k_1 a < 0. \qquad (3.38)$$

Since $\lambda_b(\tau) = 0$, it follows that, for t just less than τ,

$$\lambda_b(t) > 0. \qquad (3.39)$$

Thus, to maximise the Hamiltonian, the rate of addition must be at its maximum for t just less than τ, and so the trajectory must end with a segment of $r = r_{max}$.

On physical grounds it is expected that the initial part of the trajectory will also consist of a segment of $r = r_{max}$ in order to build up a concentration of B in the reactor.

Between these initial and terminal segments, the optimal trajectory may make use of a singular segment of the type encountered when the rate of addition was not bounded above. The meaningful part of the singular segment in this problem is that part for which $0 \leq r \leq r_{max}$.

On this singular segment $\lambda_b = 0$ and λ_a is given by equation (3.16). The rate of addition of B is given by equation (3.17), and the maximum extent of the singular segment is limited to those parts where equation (3.17) gives values of r which are within the required limits. The equation of the singular segment in the a - b plane can again be obtained by making use of the property of a constant Hamiltonian on a profile satisfying the maximum principle. In particular, the value of H on the singular segment is equal to its value at $t = \tau$:

$$H(\tau) = k_1 a(\tau)\, b(\tau). \tag{3.40}$$

Thus the equation of the singular segment in the a - b plane becomes

$$k_1 a(\tau)\, b(\tau) = -k_1 ab(\lambda_a - 1) - k_2 ab^2 \lambda_a$$

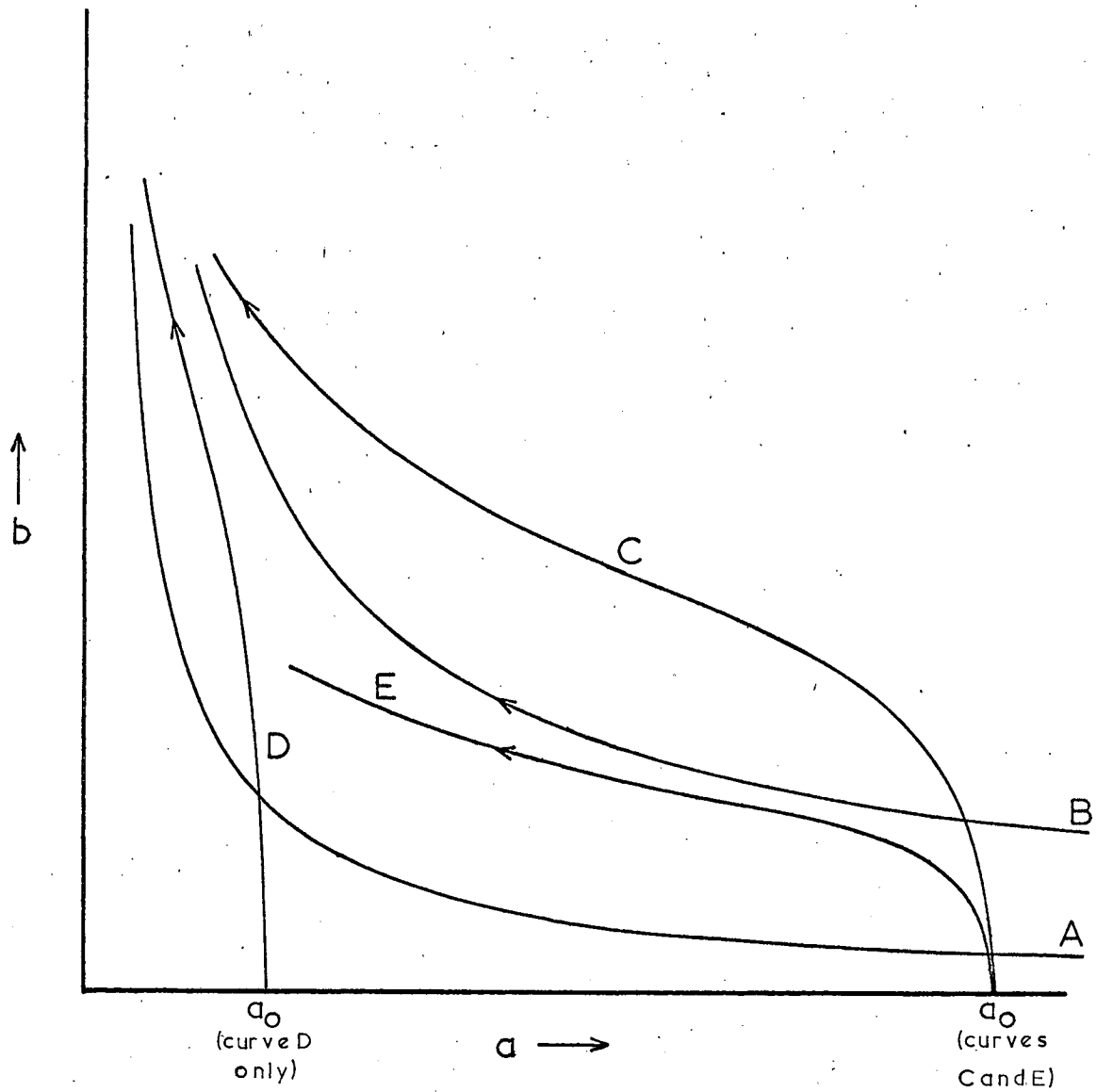
which, after substitution of equation (3.16) for λ_a, simplifies to

$$\frac{k_2 ab^2}{k_1 + 2k_2 b} = a(\tau)\, b(\tau). \tag{3.41}$$

There is a single equation of the singular segment for all sets of $a(\tau)$, $b(\tau)$ which lie on the hyperbola

$$a(\tau)\, b(\tau) = N = \text{constant}. \tag{3.42}$$

In Graph 3.4 are shown the relative positions of the terminal hyperbola of equation (3.42) (curve A) and the corresponding singular segment (3.41) (curve B) in the a - b plane. Since the concentration of reactant A decreases throughout the reaction, the locus of the point which represents the state of the reactor traces out a path from right to left in the a - b plane. It is seen that the singular segment (curve B) does not intersect the terminal hyperbola (curve A), nor does it pass through



Graph 3.4

a-b phase plane showing the terminal hyperbola of equation (3.42) (curve A), singular segment (curve B), and trajectories of $r = r_{max}$ (curves C, D and E)

the point $(a_o, 0)$. The required trajectory, therefore, must start and finish with non-singular segments, whether or not an intermediate singular segment is employed.

Curves C, D and E on Graph 3.4 show the general forms of the segments of $r = r_{max}$. These curves cross the $b = 0$ axis vertically at a_o, and may intersect the singular segment (as does curve C), but if the value of a_o or of r_{max} is too small (curves D and E respectively) for a given value of N, this intersection may not occur.

If the values of a_o, r_{max} and N are such that intersection does occur, it may be conjectured that a trajectory which satisfies the maximum principle will consist of

(1) a segment of $r = r_{max}$, from $(a_o, 0)$ in the a - b plane, leading to the singular segment, followed by

(2) a singular segment, with r given by equation (3.17), and $0 \leq r \leq r_{max}$, followed by

(3) a further segment of $r = r_{max}$, starting from the singular segment and terminating on the hyperbola given by equation (3.42).

The possibility of bang-bang type control on the non-singular segments, with r switching instantaneously between its limits, has not been eliminated by conditions imposed by the maximum principle. Confirmation as to whether such switching does occur must be obtained by numerical evaluation of the trajectory. It is also possible that a control profile which is entirely bang-bang, and makes no use of a singular segment, may satisfy the maximum principle. Again, this possibility can be confirmed or eliminated only by numerical calculation.

A suitable calculation procedure could follow the following lines. Starting from the point $(a_o, 0)$ in the a - b plane, equations (3.2) → (3.4) are integrated forwards in time with $r = r_{max}$ until the singular segment (equation (3.41)) is intersected. In order that this segment should satisfy the maximum principle, λ_b must be everywhere ⩾ 0. With λ_a given initially by equation (3.16), and λ_b initially zero, equations (3.7) and (3.8) are integrated backwards in time from the end of the non-singular segment to the beginning of the batch time.

On the singular segment the control profile can be obtained by integrating equations (3.2) → (3.4) forwards in time with r given at each point by equation (3.17). A check can be kept on the accuracy of integration by ensuring that a and b always satisfy equation (3.41) within the prescribed limits of accuracy. λ_b on the singular segment is zero, while λ_a is given by equation (3.16). Integration continues until r reaches r_{max}.

For the final postulated segment of $r = r_{max}$ to satisfy the maximum principle, λ_b must become positive on leaving the singular segment when $r = r_{max}$, passing through positive values to return to zero again at the same point as λ_a reaches zero. Trial calculations have shown that λ_b does indeed become positive on leaving the singular segment, but may return to zero either before or after λ_a reaches zero, depending on the departure point from the singular segment. An iteration procedure is therefore required to locate the position of the departure point from the singular segment so that λ_a and λ_b both reach zero at the same point. It can be easily shown that this terminal point lies on the hyperbola of equation (3.42) in the a - b plane. If the maximum principle is

satisfied throughout this non-singular final segment, then H retains its value of k_1N which it has on the singular segment. When a point of $\lambda_a = \lambda_b = 0$ is reached on this final segment, H given by equation (3.12) reduces to

$$H = k_1 ab \ ;$$

but $H = k_1N$, and so this equation reduces to

$$ab = N$$

which is identical with equation (3.42).

On the initial non-singular segment calculations have shown that λ_b does remain positive, and so no bang-bang type switching is required. For the final segment it has been possible to find a departure point on the singular segment from which integration of the state variable and adjoint variable differential equations (equations (3.2) → (3.4), (3.5) and (3.6)) gives a segment for which λ_a and λ_b reach zero simultaneously at the end point*. During this segment, λ_b remains positive, and so again no bang-bang switching occurs.

The suggested sequence of segments therefore satisfies the maximum principle if the initial segment of $r = r_{max}$ and the singular segment intersect, and the trajectory obtained may therefore be optimal for the system. The only other control policy which is known to satisfy the maximum principle is the trivial $r = 0$ everywhere, when of course there

*It has been found that, if the guess at the departure point on the singular segment is not near the required point, λ_b may never reach zero in $a > 0$, $b > 0$, and if the trial point is too far from the required point numerical instability can occur in integrating the adjoint variable differential equations. Such computational difficulties can be difficult to overcome, and can therefore prevent successful calculation of the final segment.

is no reaction.

The total batch time is given by the sum of the durations of the three segments, and it will be noticed that it is not possible to specify explicitly a batch time in the calculations of the segments. The resultant batch time is dependent on the value of N in equation (3.42), and a desired batch time must be obtained by adjustment of this value of N^*.

A complete trajectory for a given batch time is given in Graphs 3.8 to 3.10. Graph 3.8 shows r as a function of time, and it is seen that the departure point on the singular segment occurs before r reaches r_{max}. In Graphs 3.10 it is shown that λ_b is always positive on the non-singular segments, which confirms that there is no bang-bang type switching on these segments. The value Q in the caption to these graphs is the total quantity of B added.

When the initial non-singular segment does not intersect with the singular segment (e.g. curves D, E on Graph 3.4), then the control profile satisfying the maximum principle must consist of $r = r_{max}$ for all $0 \leq t \leq \tau$. Evaluation of λ_b by integration of the adjoint variable differential equations (3.7) and (3.8) backwards in time from $t = \tau$ to $t = 0$ will confirm whether this profile does in fact satisfy the maximum principle, or whether bang-bang type switching occurs. Graphs 3.5 to 3.7 show a complete trajectory for an example of such a case, and the position of the singular segment in the a - b plane is shown in Graph 3.6.

*The actual values of τ in calculations differ from the specified values by small amounts because accumulated rounding and other errors in the numerical integration of the differential equations prevented complete convergence with the iterations of N.

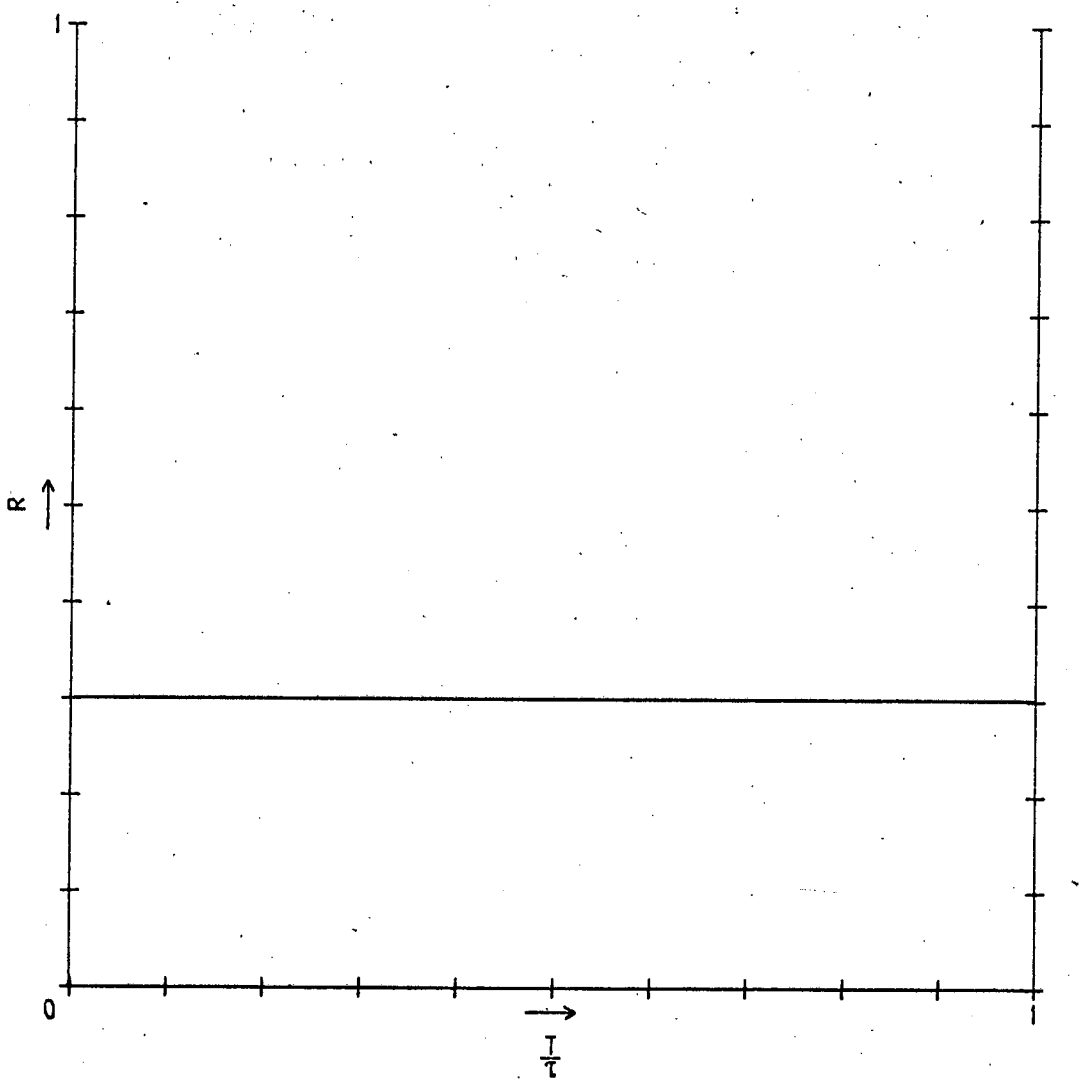
It is seen that λ_b is never negative, confirming that the profile of $r = r_{max}$ throughout satisfies the maximum principle. In this example, the value of r_{max} is smaller than for the calculation represented in Graphs 3.8 to 3.10, the other parameters being the same, and N being chosen to give nominally the same batch time.

As r_{max} is increased in value, the form of the full trajectory should logically approach closer to the trajectory obtained when there is no upper limit on r. Graphs 3.11 to 3.13 represent an example of a trajectory which satisfies the maximum principle for r_{max} greater than in the previous examples, the other system parameters being the same, and the batch time being adjusted to the same value as before. It is seen that the durations of the non-singular segments in Graph 3.11, where r_{max} is large, are somewhat less than in Graph 3.8, where r_{max} is smaller.

The value of the objective function (the final concentration of component C) should be largest when there are least constraints on the control variable when these constraints modify the shape of the final profile. The more demanding the constraint the more the objective function will be decreased. In this example it would be expected that as r_{max} is increased the value of the objective function should approach closer to the value obtained when there is no limit on r. The results of calculations for increasing values of r_{max} are summarised in Table 3.1 below. The values of the objective function have the predicted gradation, and are always less than the value obtained when there is no limit on r. The values of the objective function $c(\tau)$ are plotted in Graph 3.14.

It is seen that the values of N are not the same for different

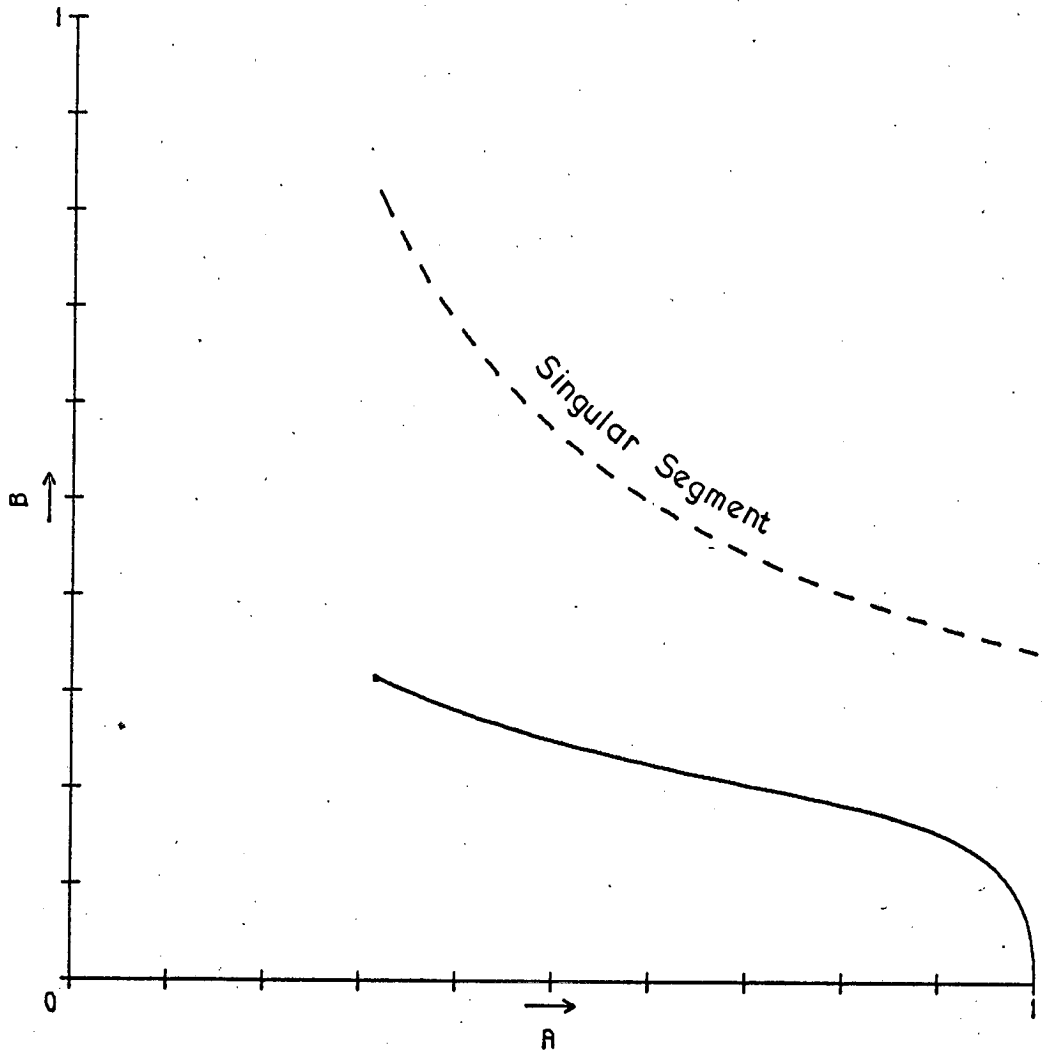
R_0 = 1.0000
R_{min} = 0.3000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.2000
τ = 4.0000
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.4843



Graph 3.5

Control policy not employing a singular segment

A_0 = 1.0000
R_{min} = 0.3000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.2000
τ = 4.0000
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.4843

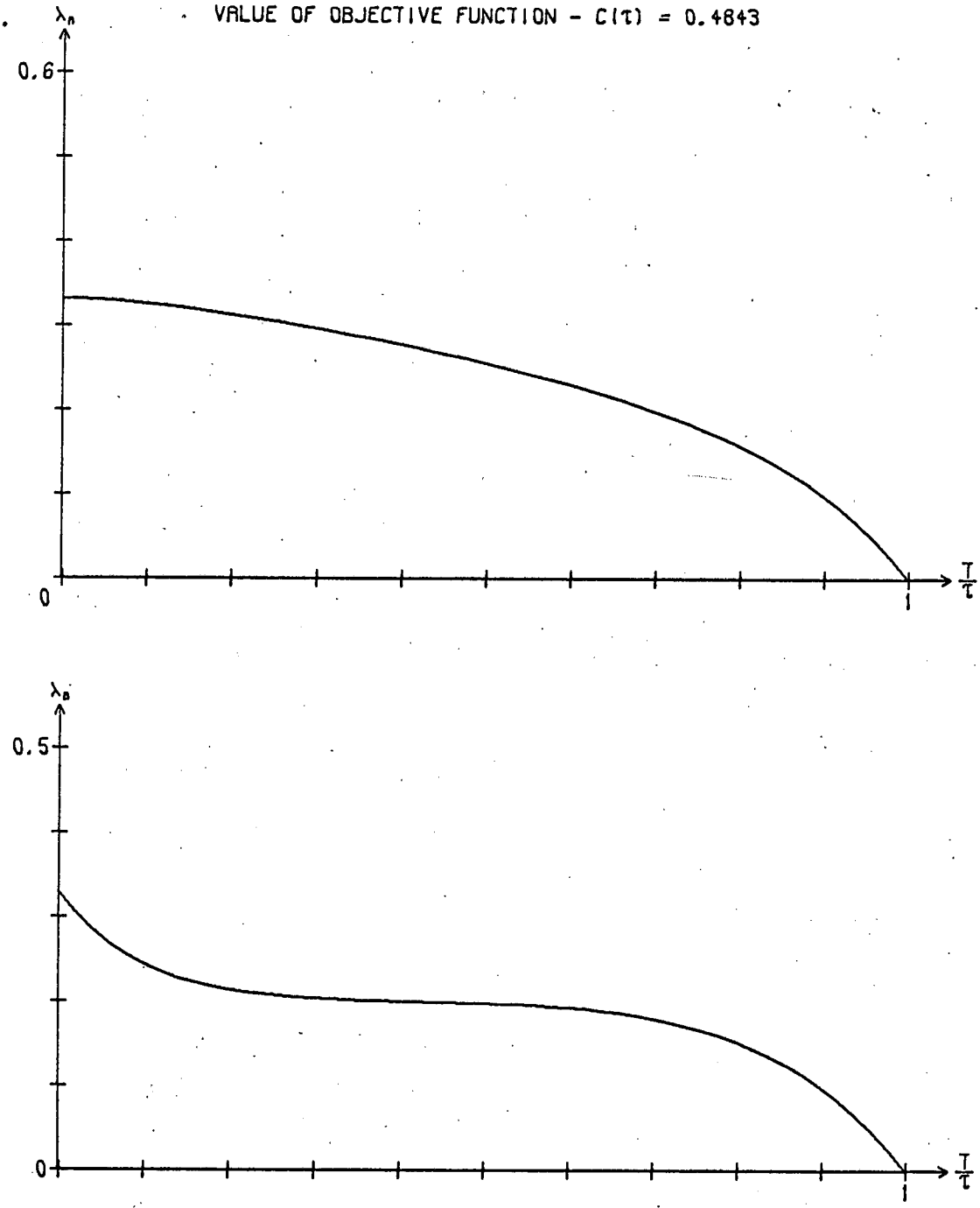


Graph 3.6

Solution trajectory in the a-b plane for the control policy of Graph 3.5, with the position of the singular segment shown

A_0 = 1.0000
R_{max} = 0.3000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.2000
τ = 4.0000

VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.4843



Graph 3.7

Adjoint variables for the control policy of Graph 3.5

A_0 = 1.0000

R_{max} = 1.0000

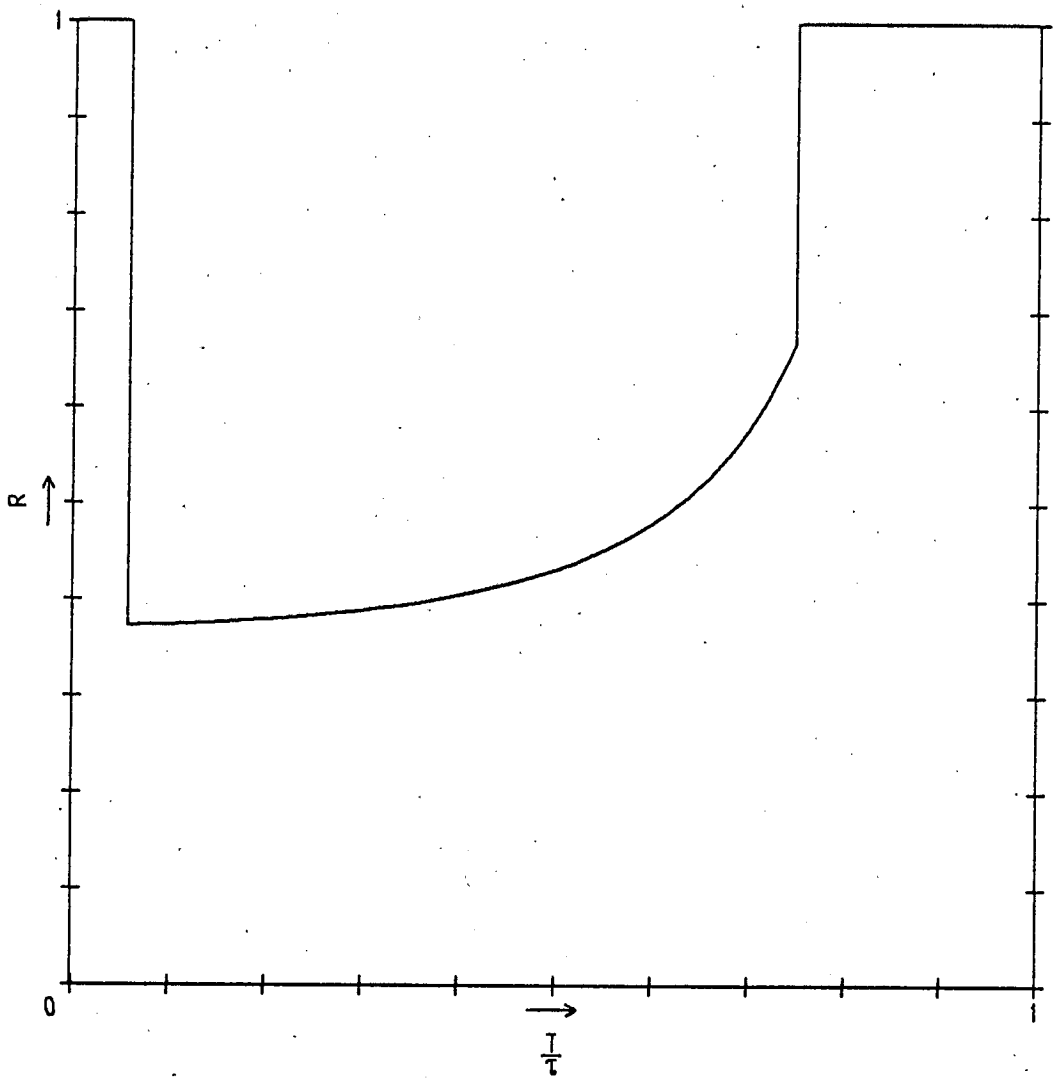
K_1 = 1.0000

K_2 = 2.0000

Q = 2.4380

τ = 3.9996

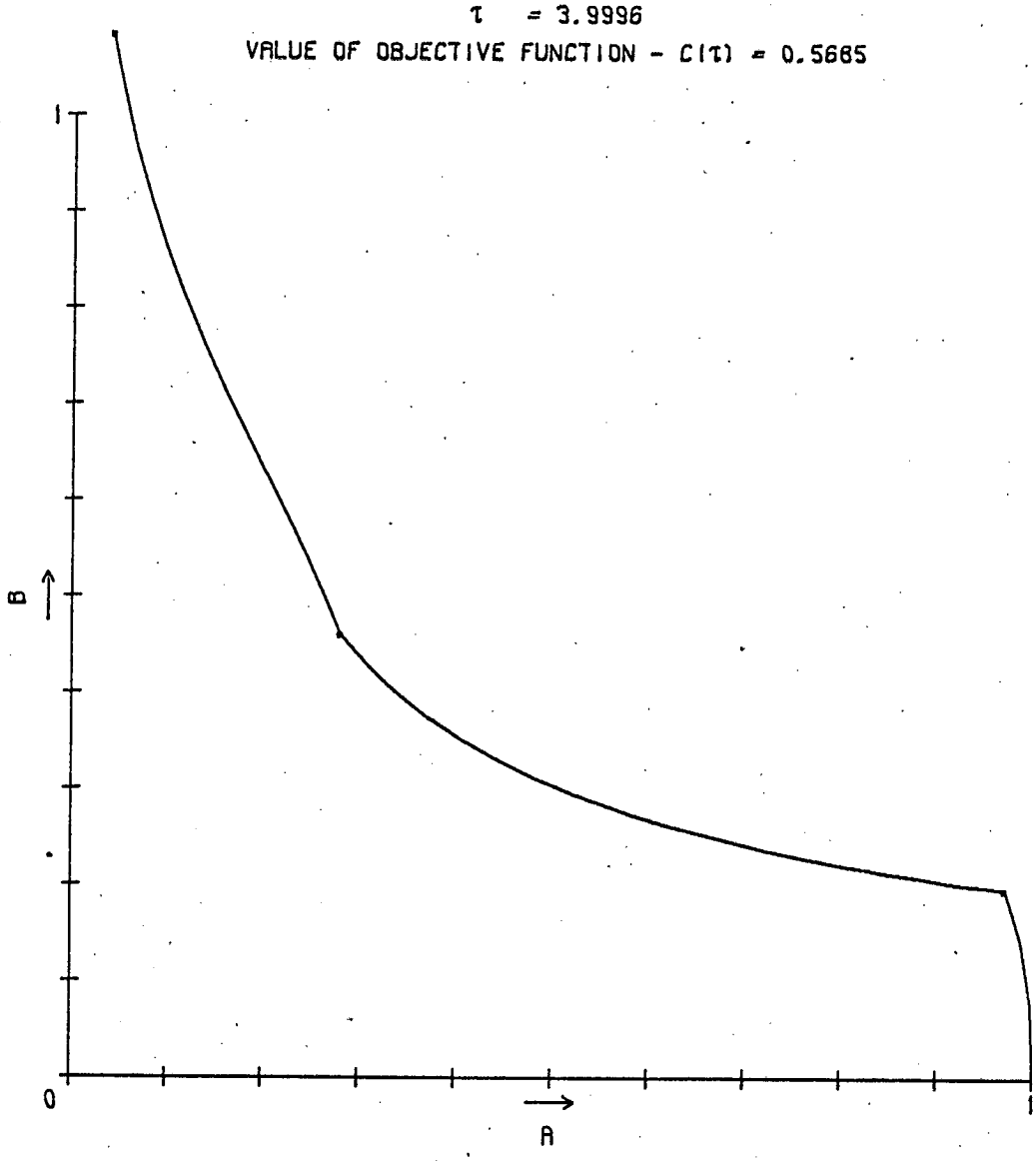
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5685



Graph 3.8

Control policy employing a singular segment

A_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4380
τ = 3.9996
VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.5665



Graph 3.9

Solution trajectory in the a-b plane for the control policy of Graph 3.8

$A_0 = 1.0000$

$R_{max} = 1.0000$

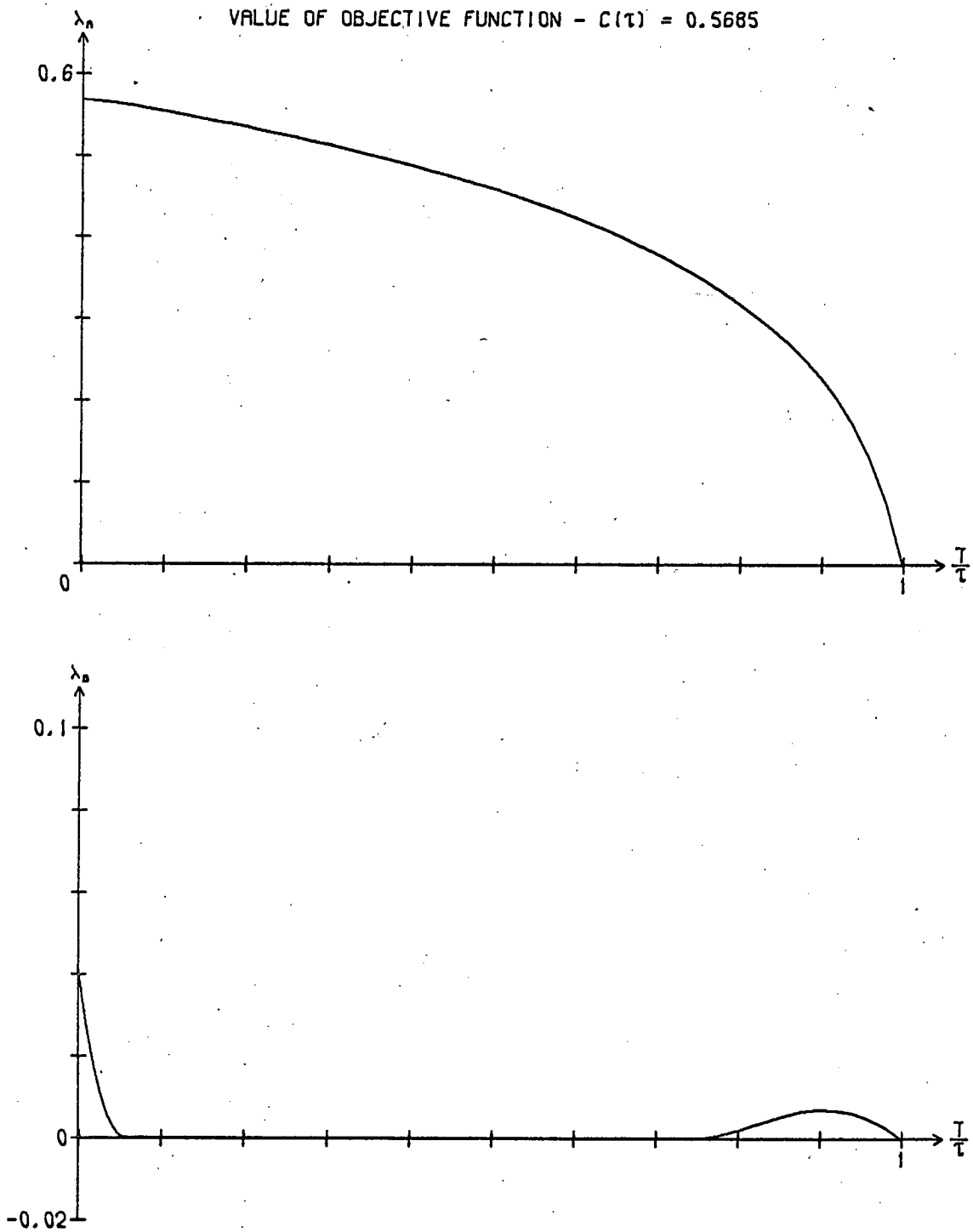
$K_1 = 1.0000$

$K_2 = 2.0000$

$Q = 2.4380$

$\tau = 3.9996$

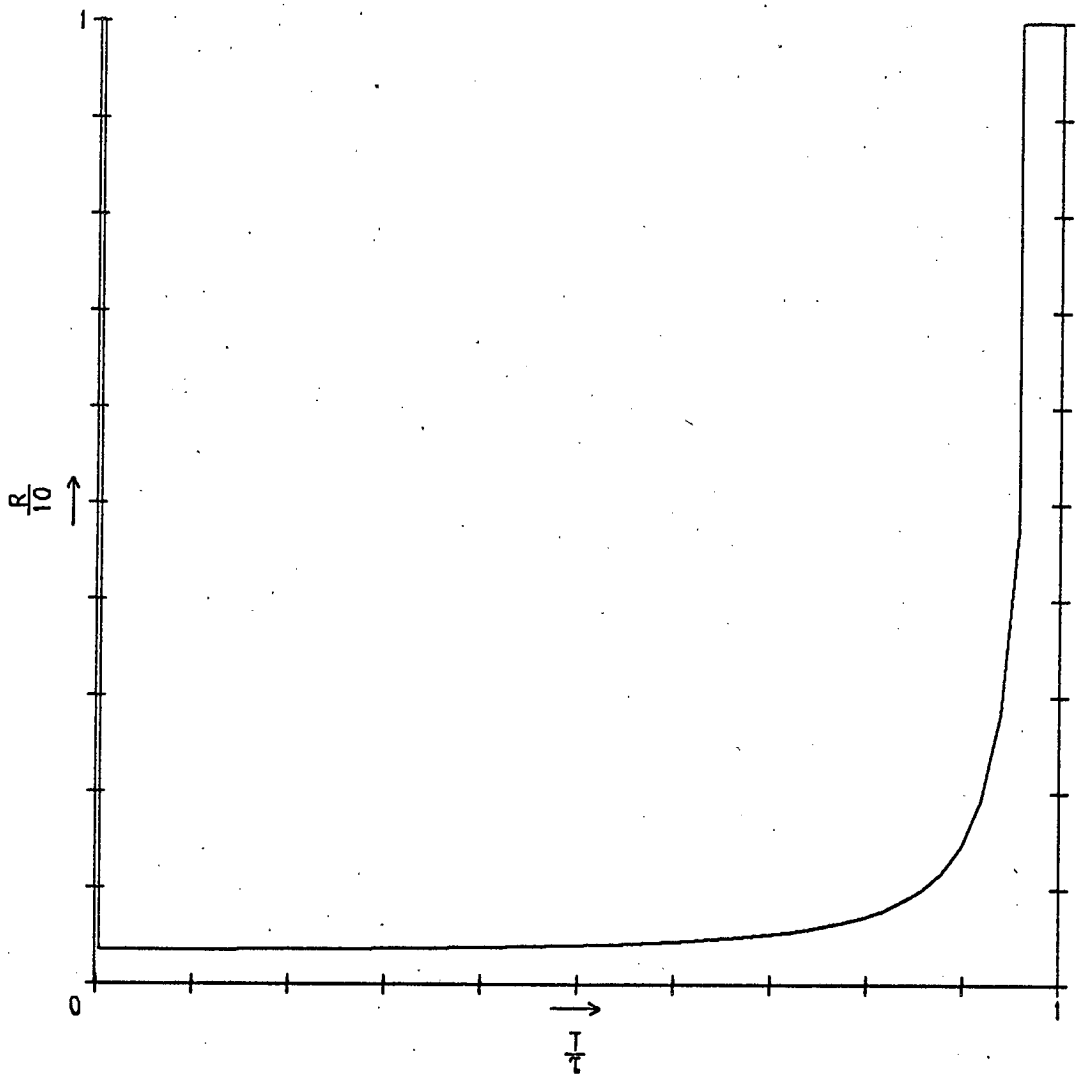
VALUE OF OBJECTIVE FUNCTION - $C(\tau) = 0.5685$



Graph 3.10

Adjoint variables for the control policy of Graph 3.8

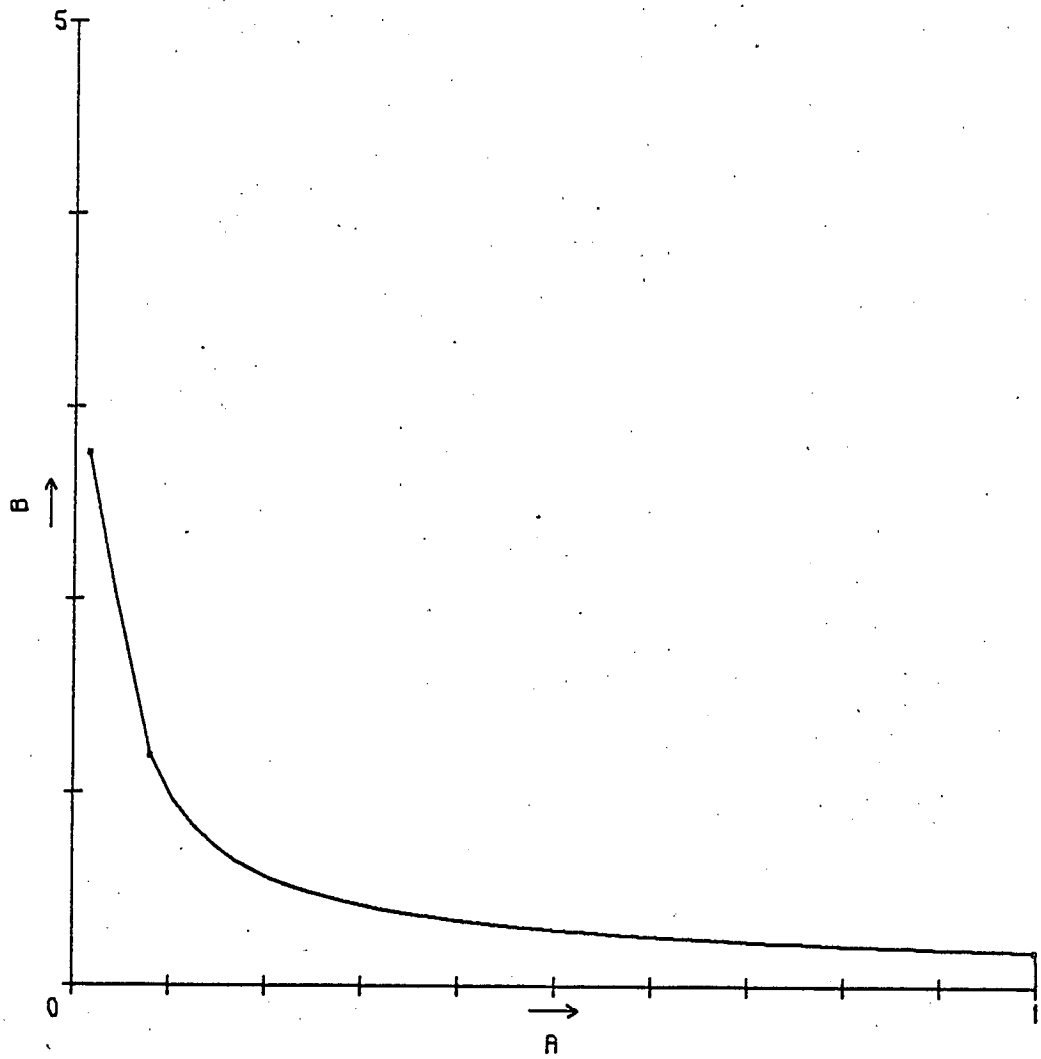
R_0 = 1.0000
R_{max} = 10.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 4.1606
τ = 3.9998
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5744



Graph 3.11

Control policy employing a singular segment, with a large value of r_{max}

A_0 = 1.0000
R_{max} = 10.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 4.1606
τ = 3.9998
VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.5744



Graph 3.12

Solution trajectory in the a-b plane for the control policy of Graph 3.11

A_0 = 1.0000

R_{max} = 10.0000

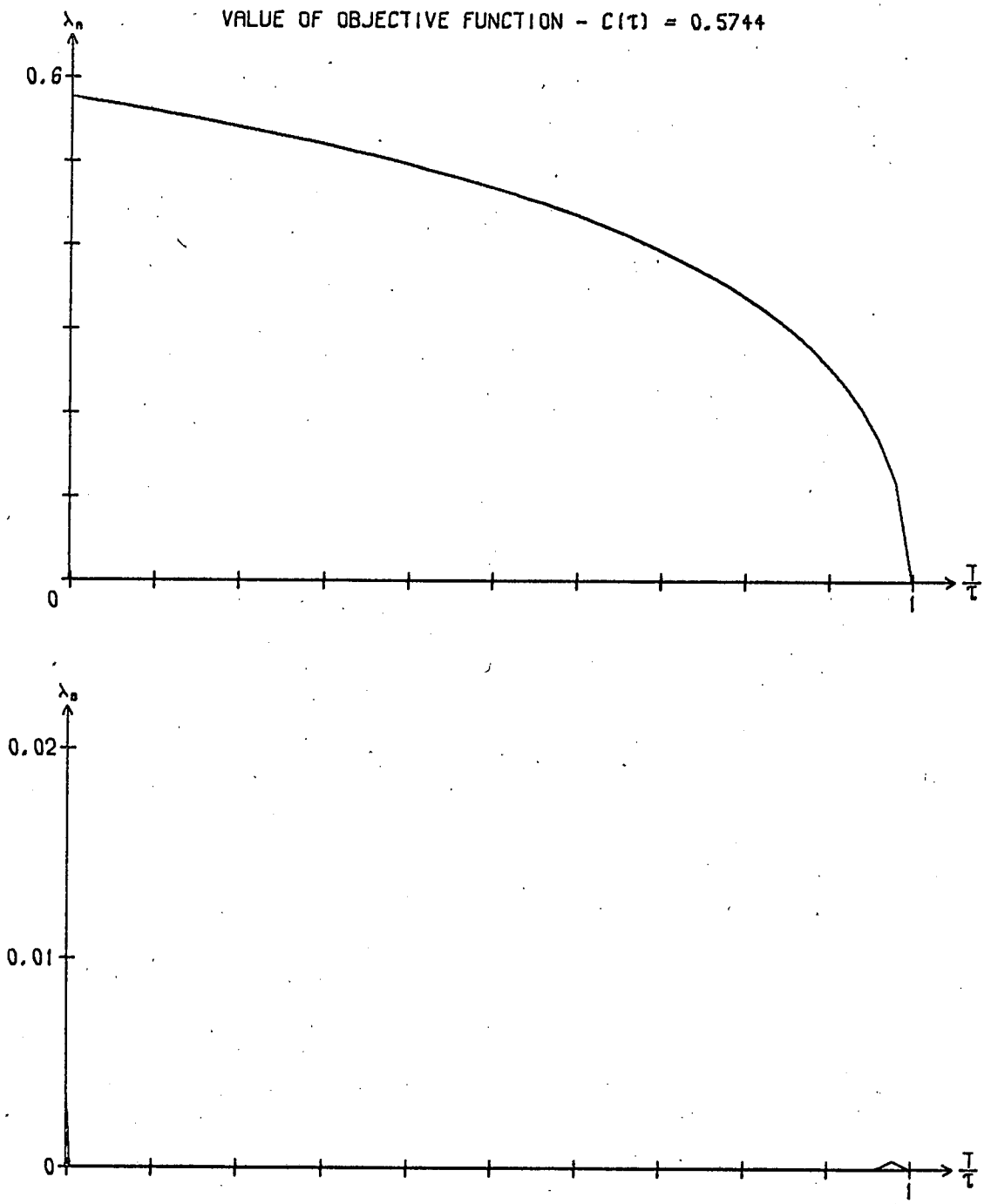
K_1 = 1.0000

K_2 = 2.0000

Q = 4.1606

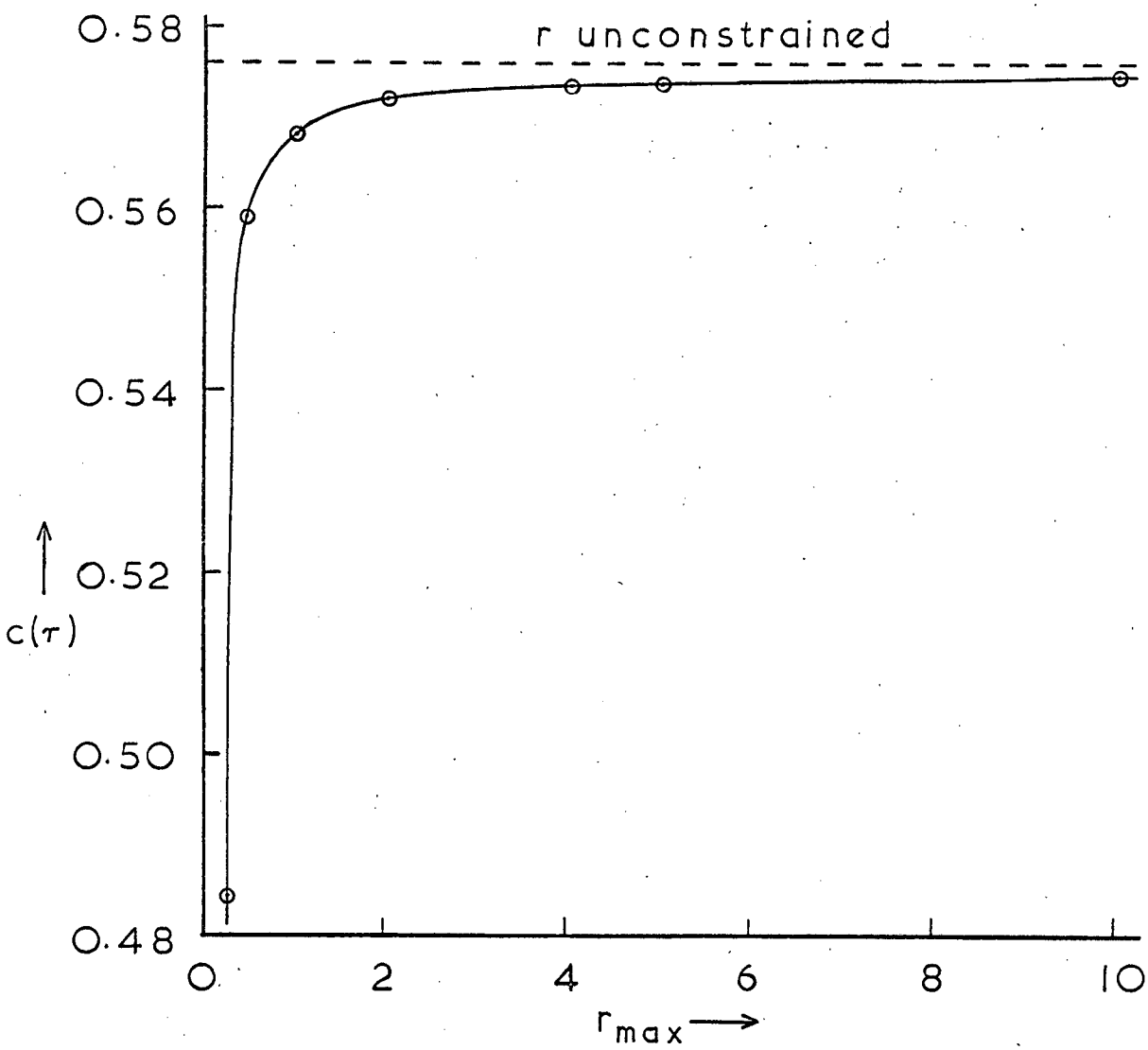
τ = 3.9998

VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5744



Graph 3.13

Adjoint variables for the control policy of Graph 3.11



Graph 3.14

Values of $c(\tau)$ for increasing values of r_{max}, and for r unconstrained. $a_o = 1$, $k_1 = 1$, $k_2 = 2$, and batch time $\tau = 4$.

Table 3.1

Summary of calculations of profiles satisfying the maximum principle for increasing values of r_{max}. $a_o = 1$, $k_1 = 1$, $k_2 = 2$, and batch time $\tau = 4$. The variable Q in this table is the total quantity of B added to the batch.

r_{max}	N	$c(\tau)$	Q
0.3	0.09930	0.4843	1.2000
0.5	0.05017	0.5590	1.9969
1.0	0.04162	0.5685	2.4380
2.0	0.04015	0.5720	2.8604
4.0	0.03957	0.5735	3.3511
5.0	0.03947	0.5738	3.5287
10.0	0.03925	0.5744	4.1606
∞	0.03906	0.5760	∞

values of r_{max}, but must vary to obtain the desired batch time. The equation for the singular segment in the a - b plane (equation (3.41)) depends on N, and since its value is different for different values of r_{max}, the singular segments are not identical. However for the larger values of r_{max} the differences in N are small, and the singular segments are then similar.

The maximum principle is only a necessary and not a sufficient condition for optimality and so, although the profiles obtained may be optimal, there may exist other profiles which also satisfy the maximum principle which give larger values of the objective function. It has

not been possible to prove that the profiles obtained are optimal, but useful confirmation can be obtained by application of a different numerical method known as the method of Gradients in Function Space.

3.2.2 Gradients in Function Space

This method, which is analogous to the method of steepest ascent in searching for a maximum of a function of a finite number of variables, is a direct numerical method of solution of the maximum principle which overcomes the problem of the two-point boundary values which occurs with the forwards and backwards numerical methods of solution described in Chapter 2. It was introduced in chemical engineering terms by Horn and Troltenier {35}, and has also been developed independently by Kelley {36}, and by Bryson and Denham {37}.

Consider a system regulated by a simple control variable u(t), which is chosen so as to maximise an objective function of the form of equation (2.3):

$$P = \sum_{i=1}^{n} \alpha_i x_i(\tau).$$

The behaviour of the system is described by differential equations (2.1), with m = 1

$$\frac{dx_i}{dt} = f_i\ (x_1, x_2, \ldots x_n, u),\ i = 1, 2, \ldots n.$$

As before, adjoint variables are introduced (equations (2.4)):

$$\frac{d\lambda_i}{dt} = -\sum_{j=1}^{n} \lambda_j \frac{\partial f_j}{\partial x_i} \qquad i = 1, 2, \ldots n.$$

Suppose that, at time t, u(t) is changed to u(t) + $\delta u(t)$ for a duration dt. Then, by Taylor expansion of equation (2.1)

$$\frac{d}{dt}\delta x_i \simeq \sum_{j=1}^{n} \frac{\partial f_i}{\partial x_j}\delta x_j + \frac{\partial f_i}{\partial u}\delta u \quad i = 1, 2, \ldots n \tag{3.43}$$

for small δu. The effect on the objective function is given by

$$\delta P = \sum_{i=1}^{n} \alpha_i \delta x_i(\tau) = \int_0^{\tau} \frac{d}{dt}(\lambda_i \delta x_i)dt \tag{3.44}$$

as $\delta x_i(0) = 0$, and $\lambda_i(\tau) = \alpha_i$ (equation (2.5)) for a maximising problem.

Now

$$\frac{d}{dt}\left(\sum_{i=1}^{n} \lambda_i \delta x_i\right) = \sum_{i=1}^{n} \lambda_i \frac{d}{dt}(\delta x_i) + \sum_{i=1}^{n} \delta x_i \frac{d}{dt}(\lambda_i).$$

By substitution of equation (3.43) for $\frac{d}{dt}(\delta x_i)$, and equation (2.4) for $\frac{d\lambda_i}{dt}$, this simplifies to

$$\frac{d}{dt}\sum_{i=1}^{n} \lambda_i \delta x_i = \sum_{i=1}^{n} \lambda_i \frac{\partial f_i}{\partial u}\delta u. \tag{3.45}$$

Hence

$$\delta P = \int_0^{\tau} \left(\sum_{i=1}^{n} \lambda_i \frac{\partial f_i}{\partial u}\delta u\right)dt. \tag{3.46}$$

An improvement in the objective function can always be obtained if the integrand is positive at each point in time, and this can be ensured by making

$$\delta u = \varepsilon \cdot \sum_{i=1}^{n} \lambda_i \frac{\partial f_i}{\partial u} = \varepsilon \frac{\partial H}{\partial u} \tag{3.47}$$

where ε is a positive parameter. $\frac{\partial H}{\partial u}$ is now a gradient function in the space of u.

The method is applied in a very straightforward manner. With a given initial control profile, the state variable equations are integrated forwards in time from $t = 0$ to $t = \tau$. Then, using the values of the state variables just obtained, the adjoint variable equations are integrated backwards from $t = \tau$ to $t = 0$. The control profile is then modified at each point in time according to equation (3.47), with a suitable value for ε, the control variable taking its limiting value when this correction takes the control variable outside its permitted range. The state variable equations can now be integrated forward in time again to obtain a new value for the objective function. There are at this stage two alternative courses of action. In the first, the adjoint variables are integrated backwards in time as before, and a new correction function obtained for the control profile. The process is then repeated until the desired convergence is obtained. This method suffers from the difficulty of choosing a suitable value of ε. If ε is too small, convergence is slow, and if ε is too large, numerical instability can occur, when divergence from the optimum instead of convergence to it tends to occur. The alternative procedure is to increase ε successively, making further improvements to the control profile with the "old" gradient function, until the value of ε is found which gives the maximum improvement in the objective function. The adjoint variables are then integrated backwards as before to obtain a new gradient function, and the procedure repeated until improvements in the objective function are within a prescribed limit. This method avoids the difficulty of

finding a suitable ε, but may involve a greater amount of computation than the other method due to the repeated forward integrations required to find ε to maximise the objective function.

The Gradients in Function Space method as described here suffers from the disadvantage that it gives only an approximation to the required control function. This is because only first order variations were considered in deriving the correction function, and the objective function is relatively insensitive to variations in the control profile near the optimum. It does however give an accurate value for the objective function {35}. There are a number of second order algorithms for correction functions {38 - 43}, but these suffer from the disadvantage that they are numerically unstable unless the initial profile is a good approximation to the optimal profile. They are therefore of little value in the present investigations.

The problem of verifying that a solution to the maximum principle is unique and therefore optimal can be overcome to some extent by the Gradients in Function Space method. If other profiles exist which satisfy the maximum principle, then these should be found by this latter method from different initial control functions. By starting with several widely differing initial control profiles it should be possible to detect whether any alternative policies exist which satisfy the maximum principle, and if only the single control profile is found then it can be considered with a degree of confidence that this is an approximation to the optimal control. If this profile approximates to that obtained by an exact solution of the maximum principle, and the value of the objective function is the same for each calculation, then

this confirms that the exact profile is optimal.

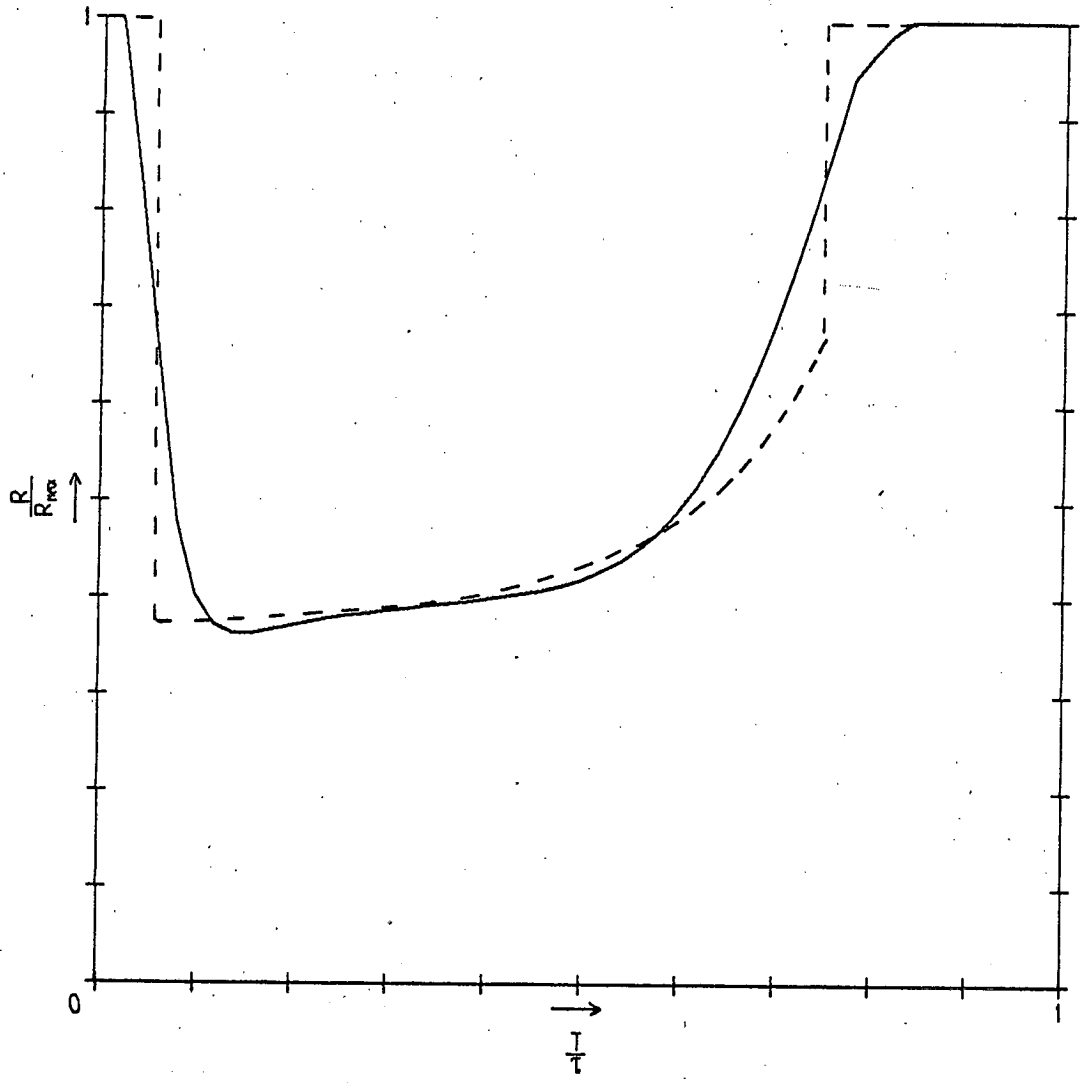
For the present problem of finding the optimal rate of addition profile, the correction function δr can be obtained by differentiating equation (3.12) with respect to r

$$\delta r(t) = \frac{\partial H}{\partial r} = \lambda_b . \tag{3.48}$$

Using an initial profile of $r = r_{max}$ for $0 \leqslant t \leqslant \tau$, calculations were made for $r_{max} = 1$, and other parameters as for previous calculations. Adjoint variables were integrated and a new correction function evaluated after each forward integration of the state variables, ε being halved when a decrease in the objective function occurred. This method was found to involve somewhat less computation and converged more quickly once a suitable initial value for ε was found. The resulting trajectory is shown in Graphs 3.15 to 3.17, in which the trajectory for the exact solution for corresponding r_{max} (Graphs 3.8 to 3.10) is shown as broken lines for comparison. The value of the objective function after each "ascent" is shown in Graph 3.18, where it is seen that convergence is quite fast. The initial value of ε was 1.0.

It is seen immediately that the step discontinuities obtained in the exact solution are "rounded off" and therefore effectively concealed by the Gradients in Function Space method of solution. However the resemblance is close, and the value of the objective function, 0.569, compares within the limits of accuracy of calculation to the value 0.5685 obtained by the exact solution (integrations were to an accuracy of better than 1 in 10^4 for each step, there being approximately 100 steps for both the exact solution and the Gradients in Function Space method).

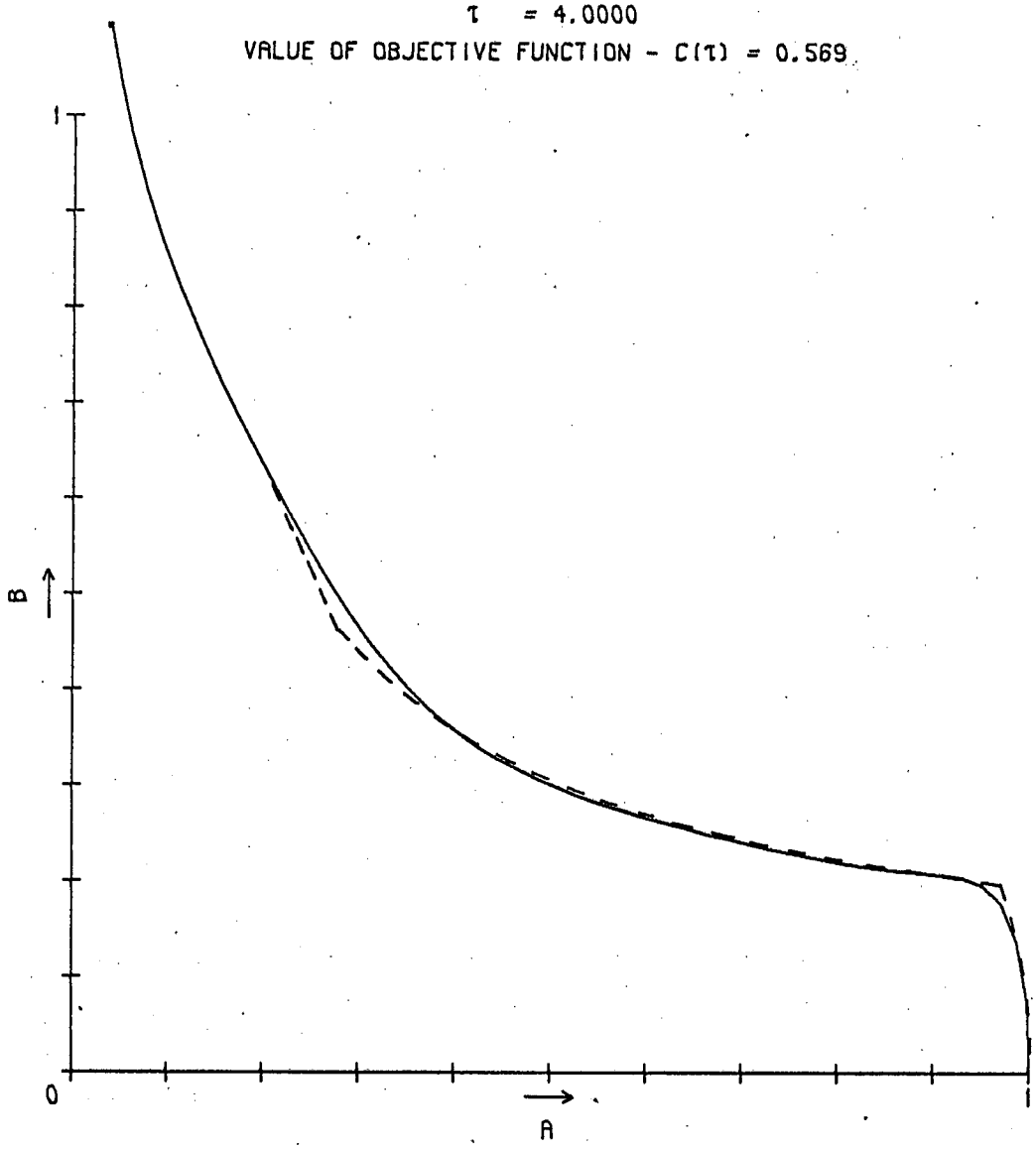
A_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4529
τ = 4.0000
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.569



Graph 3.15

Control policy derived via the method of Gradients in Function Space. The exact solution is shown in broken lines for comparison.

A_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4529
τ = 4.0000
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.569

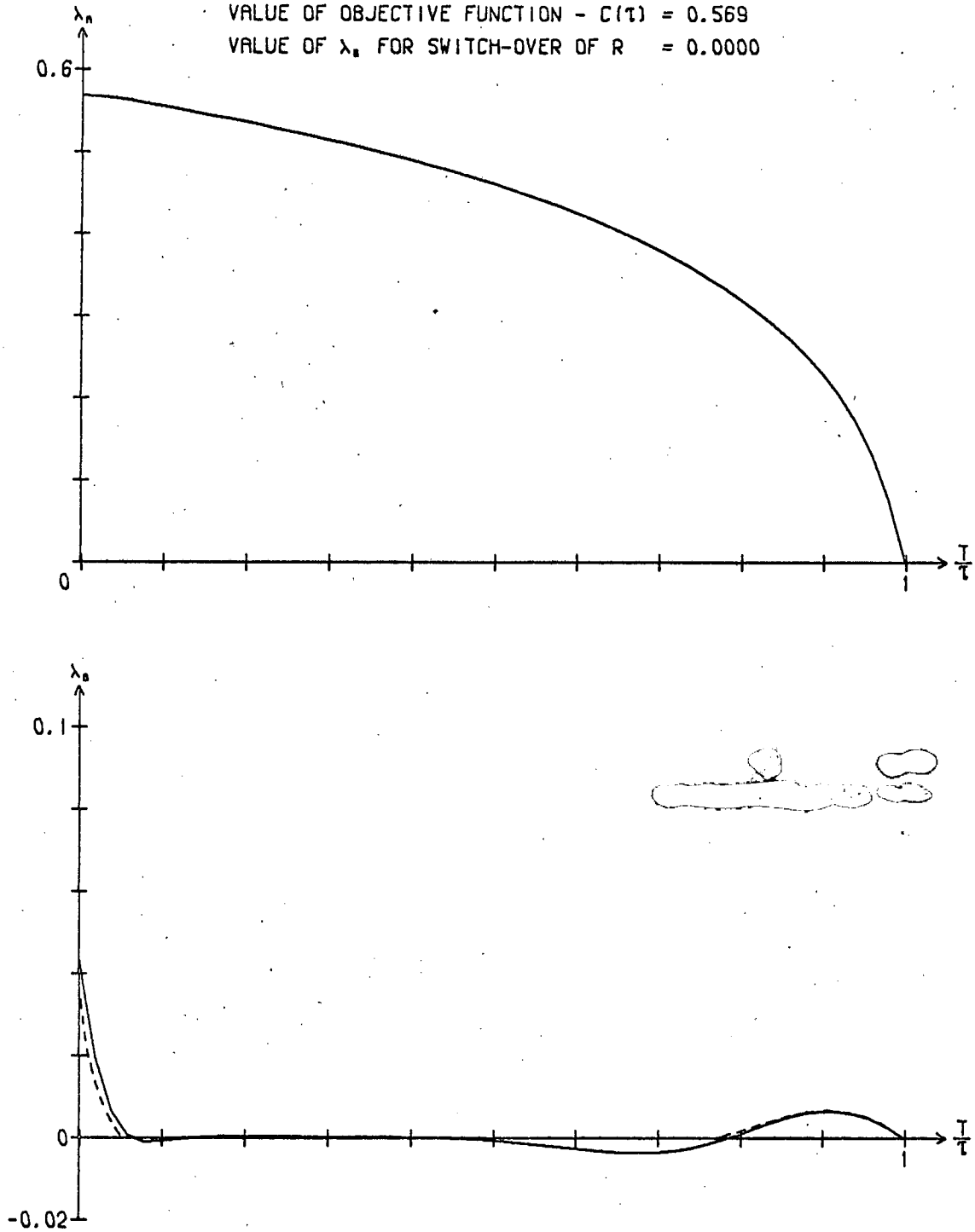


Graph 3.16

Solution trajectory in the a-b plane for the control policy of Graph 3.15. The exact solution is shown for comparison as a broken line where it deviates from this graph.

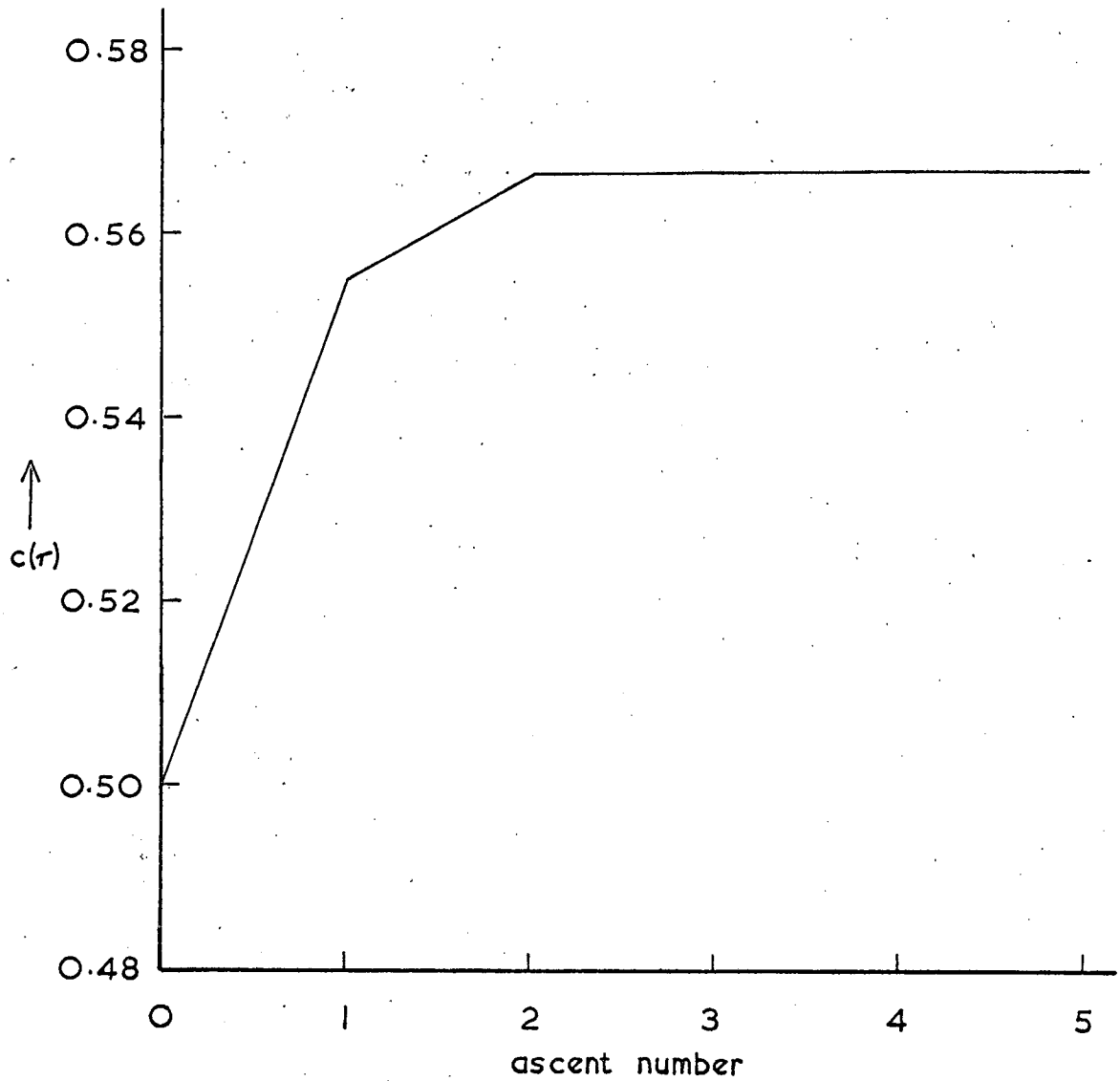
R_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4529
τ = 4.0000

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.569
VALUE OF λ_a FOR SWITCH-OVER OF R = 0.0000



Graph 3.17

Adjoint variables for the control policy of Graph 3.15. The λ_a profile is close to the profile for the exact solution. Deviations of the exact solution from the λ_b profile are shown as broken lines.

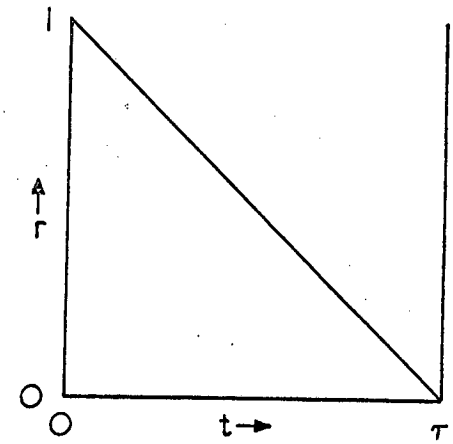


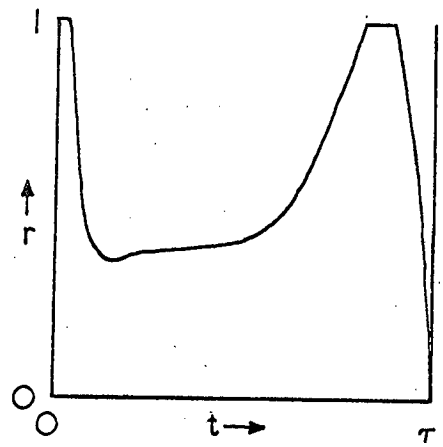
Graph 3.18

Values of $c(\tau)$ on successive ascents in the Gradients in Function Space method of solution.

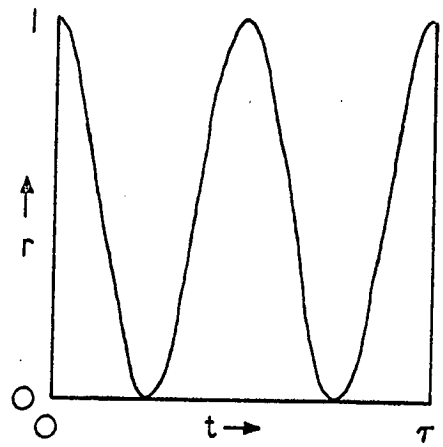
initial profiles

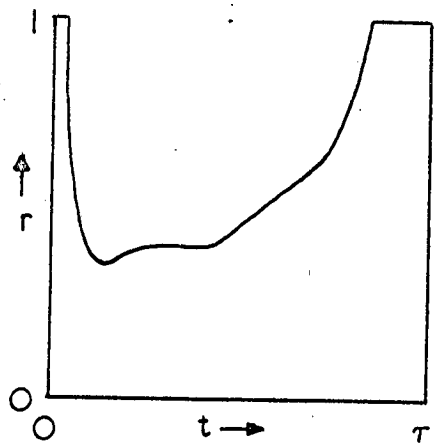
final profiles



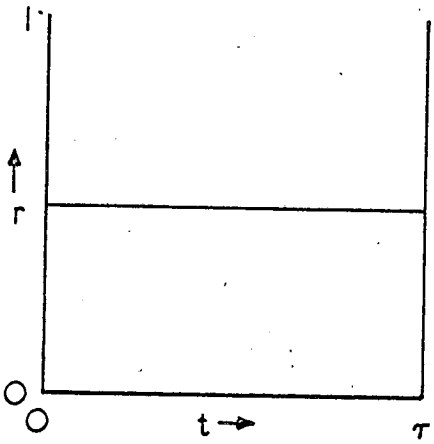


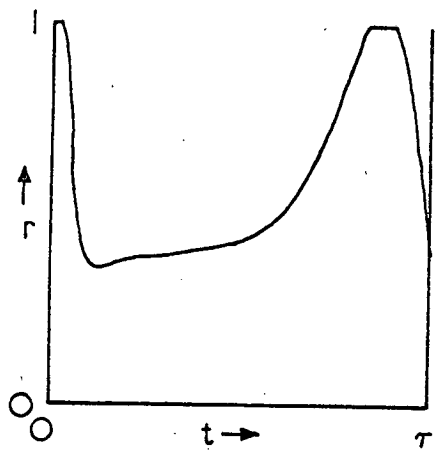
(a) Value of objective function = 0.569





(b) Value of objective function = 0.569





(c) Value of objective function = 0.569

Graph 3.19

Graphs of different initial and resultant final control profiles for Gradients in Function Space searches for the optimal rate of addition policy. $a_o = 1$, $k_1 = 1$, $k_2 = 2$, $r_{max} = 1$, and batch time $\tau = 4$.

As a check that this profile was the only one satisfying the maximum principle, a number of different initial profiles were used. These initial profiles, the resulting final profiles and the values of the objective function obtained are given in Graph 3.19. Because $\lambda_b \to 0$ at $t \to \tau$, the correction function $\delta r \to 0$ as $t \to \tau$. As a result, if the initial profile terminates with other than r_{max} (which is the required terminal value of r on the optimal profile) the final profile from a Gradients in Function Space search tends towards the initial profile at $t \to \tau$. This effect is shown in Graphs 3.19(a) and 3.19(c), and this difference in the shape of the final control profile is therefore not significant.

It can be seen that, apart from this approximation, the final profiles of Graphs 3.19 have the same general shape, and the values of the objective function are the same within the accuracy of calculation. It can be concluded that there is almost certainly only one control profile which satisfies the maximum principle (apart from the trivial $r = 0$ throughout), and that this control profile is therefore optimal.

3.3 Discussion

It was noted that in equation (3.12) the Hamiltonian is linear in r, and that in such circumstances a singular segment may be possible. Whenever a Hamiltonian function is formed which is linear in one of the control variables, the system must be examined further to determine whether singular control is possible. Even if it is found to be permissible, however, it is not necessary that the solution trajectory should

make use of a singular segment; a bang-bang policy may satisfy the maximum principle. For example, in investigating the time-optimal control of a C.S.T.R., with an exothermic reaction, to its steady state by means of varying the heat removal rate, Siebenthal and Aris {30} pointed out that alternative control profiles may exist, both satisfying the maximum principle, one of which contains a singular segment and one of which is bang-bang. The determination of which policy is optimal must be made by numerical evaluation of the time to reach steady-state for each control policy. Paynter and Bankoff {44}, in their investigation of the optimal heat transfer coefficient design along a tubular reactor with recycle, also observed that a singular segment might form part of the optimal profile, but in this case only a bang-bang policy was found to satisfy the maximum principle.

In chemical engineering applications of the maximum principle, singular segments appear to feature quite regularly. In addition to the examples already mentioned, the optimal control of reactors by distributed additions of cold feed studied by Dyson and Horn {14} and Dyson and Graves {15} involves a singular segment in the optimal control. In the problem of optimal catalyst blend of a bifunctional catalyst {45, 46, 49}, Jackson {47} has shown that the application of the maximum principle leads to a solution trajectory which may have a singular segment as an intermediate part of the optimal profile, although a bang-bang solution may also satisfy the maximum principle.

When an optimal control profile consists of bang-bang control, or when it makes use of singular control, it is not difficult to see why computational difficulties occur when a direct numerical attack is made

by the forwards or backwards method on the solution of the maximum principle. In such situations, deductions from the maximum principle of the form of the required control must be made before any form of numerical solution can be made with any hope of success.

In the examples given in this chapter of determining the rate of addition policy which satisfies the maximum principle, it is possible to deduce a large amount about the required control profile, to the extent of an almost entirely analytical solution for the case of no upper limit on r. In more complicated examples it may not be possible to deduce as much information. In such circumstances the method of Gradients in Function Space may be used to give some further insight into the final solution, but, because of the approximate nature of this method of solution in the form described in this chapter, essential features of the exact solution may be concealed, or features may appear which do not exist in the exact solution. By extending the derivation of the correction function to include second order variations {38 - 42} a more exact solution may be obtained. The instability which occurs when a second order Gradients in Function Space method is used with a poor initial approximation to the control profile may be overcome by a method suggested by Lapidus and Luus {43}, in which an approximation to the required control profile is obtained by a first order Gradients in Function Space search, and this approximate profile is used to initiate a 2nd order search using Merriam's {39, 40} algorithm.

The main value of the Gradients in Function Space method, however, is in confirming that a control profile derived by some exact method is optimal, and in the example given in this chapter this confirmation is convincingly achieved.

CHAPTER 4

SOME EXTENSIONS TO THE BASIC PROBLEM OF FINDING THE OPTIMAL ADDITION-RATE PROFILE

The problem in Chapter 3 has been framed in the simplest possible terms, with no constraint on the total amount of B to be added, other than, in the second section of Chapter 3, the ~~implicit~~ limit implied by the bound on the maximum rate of addition. In a practical situation it may be desired to specify the total amounts of each reactant to be added to the reactor batch. This limitation on the system may be imposed in conjunction with the constraint on the maximum rate of addition of reactant, but since this latter constraint was originally imposed in order to limit the amount of reactant added to a finite level, it will also be interesting to consider the effect on the control profile of removing this limit on r_{max}. The reactor system investigated in the previous chapters will now be re-examined, with these modifications imposed.

4.1 Specifying The Total Amount of Reactant B Added, With r Bounded Above

4.1.1 Theoretical Considerations

If it is wished to specify the quantity of B to be added, Q, to the reactor during the interval $0 \rightarrow \tau$, it is necessary to introduce a further variable q, whose value at a time t represents the amount of B added during the interval $0 \rightarrow t$. The variable q must therefore satisfy

the following differential equation and boundary conditions

$$\frac{dq}{dt} = r; \quad q(0) = 0; \quad q(\tau) = Q \ (< \tau\, r_{max}). \tag{4.1}$$

Associated with q is an adjoint variable μ, which is subject to

$$\frac{d\mu}{dt} = 0. \tag{4.2}$$

Since the terminal value of q is specified, there is no specified boundary value on μ (c.f. equation(2.9)). It follows from equation (4.2) that μ is constant, and its constant value will be denoted by γ. Since the choice of γ has no influence on the values of the other adjoint variables, it is free to be chosen in order to satisfy the terminal boundary condition on q.

The Hamiltonian now has the form

$$H = (\lambda_b + \gamma)r - k_1 ab(\lambda_a + \lambda_b - 1) - k_2 ab^2(\lambda_a + 2\lambda_b) \tag{4.3}$$

where $\lambda_c(t)$ is again equal to 1 (equation (3.11)). It follows from equation (3.10) (the boundary conditions on the adjoint variables) that, at $t = \tau$, the Hamiltonian is given by

$$H_\tau = \gamma r + k_1\, a(\tau)\, b(\tau). \tag{4.4}$$

This is maximised by $r = 0$ or $r = r_{max}$ depending on whether γ is negative or positive respectively. When $\gamma = 0$, the system corresponds to that for which $q(\tau)$ is unspecified, when it has already been seen that $r = r_{max}$ at $t = \tau$. Thus the Hamiltonian is maximised by

$$\left.\begin{array}{ll} r = r_{max} & \text{for } \gamma \geqslant 0 \\ r = 0 & \text{for } \gamma < 0 \end{array}\right\} \text{ at } t = \tau. \tag{4.5}$$

If a modified signum function is introduced such that

$$\begin{aligned} \text{sgn } 1(\gamma) &= 0 \text{ for } \gamma < 0 \\ \text{sgn } 1(\gamma) &= 1 \text{ for } \gamma \geqslant 0 \end{aligned} \tag{4.6}$$

then the maximum value of H_τ, which is the maximum value of the Hamiltonian for all $0 \leqslant t \leqslant \tau$ when the maximum principle is satisfied, is given by

$$H_{max} = k_1 N + \gamma r_{max} \text{ sgn } 1(\gamma) \tag{4.7}$$

where the substitution of equation (3.42) for $a(\tau)\ b(\tau)$ has been made.

As for previous problems, the Hamiltonian is again linear in the control variable, r. Therefore a singular segment can occur, for which the necessary conditions are

$$\lambda_b = -\gamma \tag{4.8}$$

and

$$\frac{d\lambda_b}{dt} = 0 . \tag{4.9}$$

Expanding these conditions as before, by substituting equation (3.8) into (4.9), and substituting equations (3.11) and (4.8) throughout leads again to an expression for λ_a

$$\lambda_a = \frac{k_1 + \gamma(k_1 + 4k_2 b)}{k_1 + 2k_2 b} . \tag{4.10}$$

Differentiating this

$$\frac{d\lambda_a}{dt} = \frac{2k_1 k_2(\gamma - 1)}{(k_1 + 2k_2 b)^2} \frac{db}{dt} . \tag{4.11}$$

Substituting for $\frac{db}{dt}$ (equation (3.3)) and comparing the result with equation (3.7), it then follows that, provided $\gamma \neq 1$,

$$r = b(k_1 + 2k_2 b)(a + \tfrac{b}{2}) \tag{4.12}$$

which is identical with equation (3.17). It will be shown below that γ is always less than 1.

An expression for the Hamiltonian on the singular segment is obtained by substitution of the expression for λ_a (equation (4.10)) and λ_b (equation (4.8)) on the singular segment into equation (4.3). The value of H on the singular segment must be the same as its value on any other part of the trajectory if the maximum principle is to be satisfied, and an expression for the maximum value of the Hamiltonian at $t = \tau$ has already been obtained (equation (4.7)). Comparing this with the value of the Hamiltonian on the singular segment leads to an equation for the singular segment in the a - b plane as before

$$\frac{k_2 ab^2 (1 - \gamma)}{k_1 + 2k_2 b} = N + \frac{\gamma r_{max} \text{ sgn } 1(\gamma)}{k_1} . \qquad (4.13)$$

It is now seen why γ can never be as great as 1 if the singular segment is to form part of the optimal trajectory; for if a value of 1 or greater is substituted for γ in equation (4.13), the left hand side becomes zero or negative, and then no finite positive values of a and b can be found which satisfy this equation.

The equation (4.13) has a similar shape in the a - b plane to curve B of Graph 3.4, and again does not pass through the initial point $(a_o, 0)$, nor does it intersect with the terminal hyperbola (curve A). Thus the overall situation is similar to that when Q is unspecified, and the solution trajectory is again likely to consist of 3 segments

(1) initial non-singular segment, with $r = r_{max}$

(2) singular segment, with r given by equation (4.12)

(3) final non-singular segment.

The final segment in this case, however, may have $r = r_{max}$ or $r = 0$, depending on the value of γ. When γ is very near to zero the full trajectory should logically be similar to the trajectory obtained when Q was unspecified (when $\gamma = 0$), and in particular the final segments should not differ greatly. When $\gamma > 0$ the final segment must end with $r = r_{max}$ (equation (4.5)), and the final segment should therefore logically be $r = r_{max}$ throughout. It seems likely that this form of the final segment will extend to all permissible values of $\gamma > 0$. When $\gamma < 0$, the final segment must end with $r = 0$, but, if the final segment for γ just less than zero is to be similar to that for $\gamma = 0$, r must switch from r_{max} to zero near to $t = \tau$.

When γ is negative it is likely that the quantity of B used in the reaction will be less than for $\gamma = 0$, since a negative value of $\mu(\tau)$ is equivalent to costing B in the objective function

$$P = c(\tau) + \gamma q(\tau), \ \gamma < 0 \ . \qquad (4.14)$$

If B is costed then this would logically have the influence of decreasing the quantity of B used. Conversely, if γ is positive, the quantity of B used will be greater than that used when $\gamma = 0$. Thus, in order to obtain the desired value of Q when calculating the solution trajectory, adjustments in the value of γ will have to be made.

It follows from consideration of equation (4.14) that γ can never be as small as -1. Such a value for γ would be equivalent to 1 unit of B costing the same as the selling value of 1 unit of C; but since in this reaction system 1 unit of B always produces considerably

less than 1 unit of C, there could never be a profit, and the reactor would be run with least loss if it does not operate at all, i.e. $r = 0$ throughout. It has also been shown that, for a singular segment to form part of the solution trajectory, $\gamma < 1$. Therefore γ must be chosen within the range $-1 < \gamma < 1$ in order to obtain the desired value of Q.

The calculation procedure for the required trajectory would be of the following form. The initial and singular segments are calculated in the same fashion as before for specified values of reaction parameters and assumed values for N and γ. A departure point from the singular segment is found for the final segment by an iterative method as before, the value of r on this segment being governed by the values of λ_b and γ.

Having obtained a solution trajectory in this way, the values of Q and τ obtained will not generally be as required. It has already been suggested that the value of Q can be adjusted by varying γ, keeping N constant, but this also affects the batch time. Similarly if N is adjusted to obtain the desired batch time, with γ remaining unchanged, the value of Q obtained varies slightly, requiring compensation of the value of γ, to obtain the same value of Q. Thus to obtain the required combination of batch time and Q simultaneous iteration on N and γ is required, and since for each iteration a complete solution trajectory must be evaluated, a considerable amount of computation is required.

The correct initial value of r on the final non-singular segment at the departure point from the singular segment must be found by trial and error. Calculations have shown that $r = r_{max}$ initially for $\gamma \geqslant 0$ and for γ only slightly negative; for γ more negative, $r = 0$

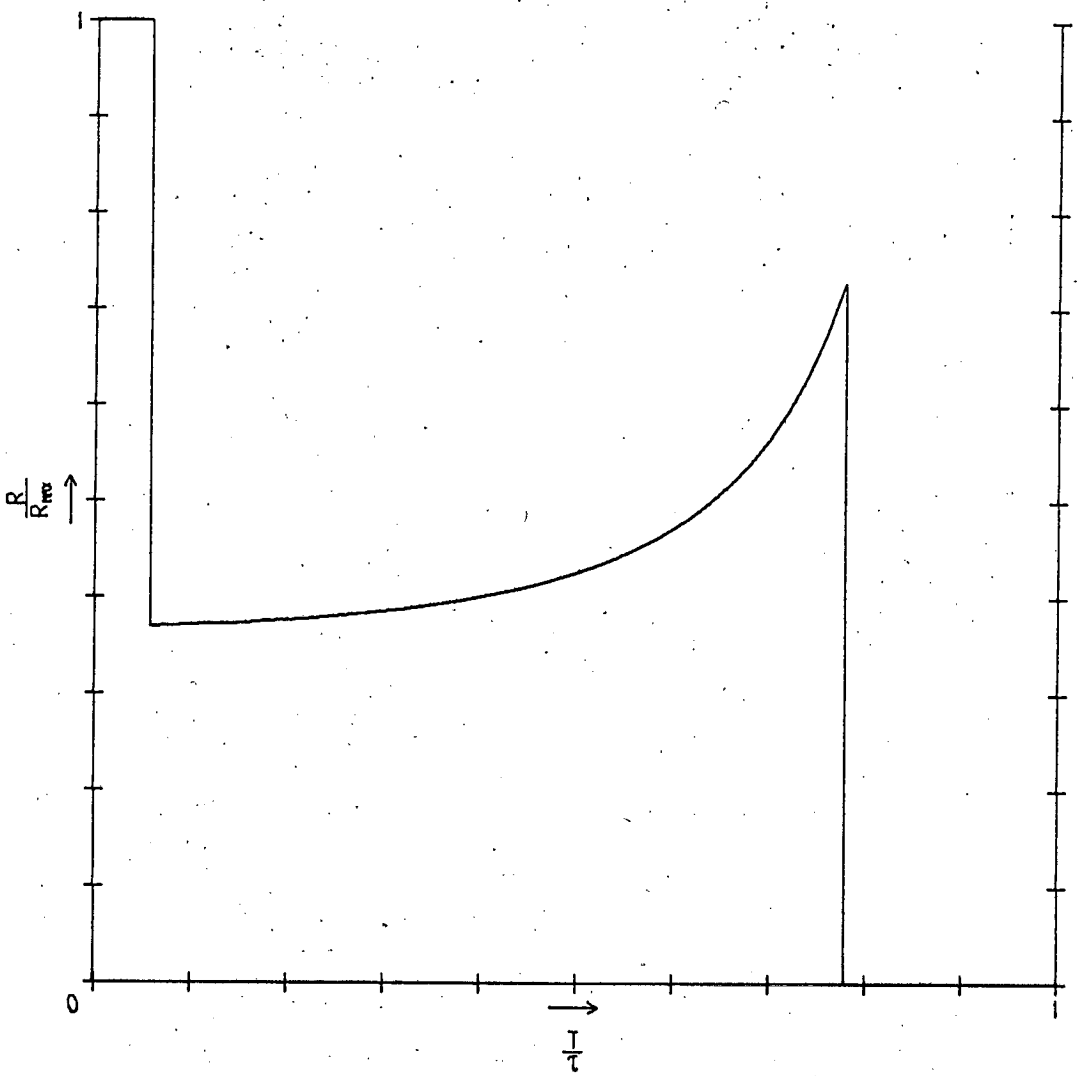
initially, and the final segment consists of r = 0 throughout. If the wrong initial value for r is taken, the value of λ_b may force r immediately to the correct value, in which case there is no real difficulty. However, in some cases, if the wrong initial value of r is taken, it has been found that λ_a may never reach zero, or that λ_b may never reach zero, for any departure point from the singular segment. When such a situation occurs, r must be set initially to the other limiting value and the search for the departure point from the singular segment repeated.

4.1.2 Results of Calculations

The same reaction parameters as for the examples in Chapter 3 were used, viz. $a_o = 1$, $k_1 = 1$, $k_2 = 2$ and batch time $\tau = 4$. For a value of $r_{max} = 1$, the value of Q obtained (Graphs 3.8 - 3.10) was 2.4380, and so calculations were made with this same value of r_{max} for values of Q between 1.2 and 2.7. The values of τ and Q in these calculations are nominal, since accumulated approximations in the calculations of the solution trajectories prevented complete convergence in the iteration procedure on N and γ. The actual values of τ and Q are recorded on the graphs of the resulting trajectories.

The solution trajectory for Q = 1.5 is shown in Graphs 4.1 to 4.3, and it is seen that the final non-singular segment is a "coasting" segment of r = 0 throughout. For Q = 2.0 (nominally) (Graphs 4.4 to 4.6), the final segment is in two parts, with $r = r_{max}$ initially, and r switching to zero before $t = \tau$. For these two sets of results, $\gamma < 0$

R_0 = 1.0000
R_{MAX} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.5000
τ = 3.9999
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5474

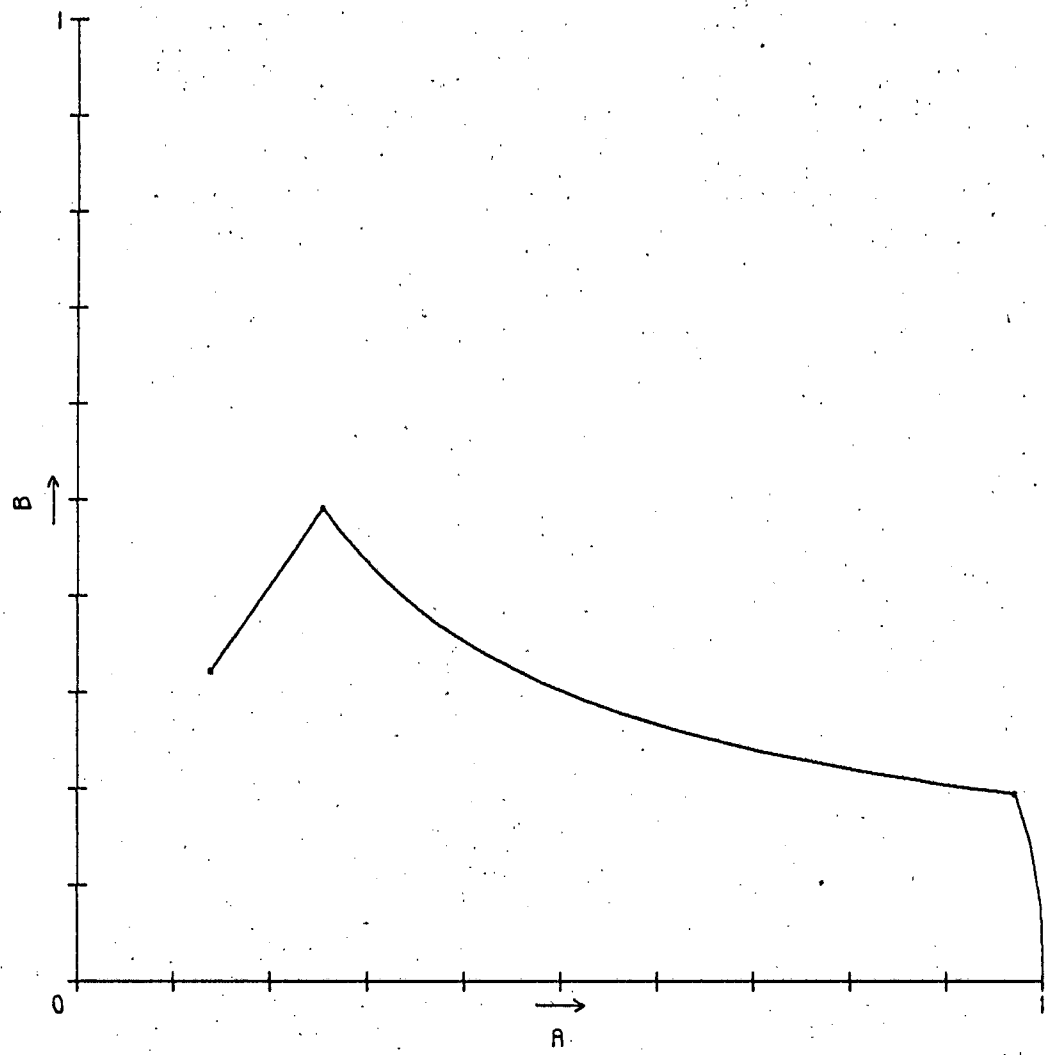


Graph 4.1

Control policy for Q specified and r constrained.
The value of Q is nominally 1.5

A_0 = 1.0000
R_{MAX} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.5000
τ = 3.9999

VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5474



Graph 4.2

Solution trajectory in the a-b plane for the control policy of Graph 4.1

$A_0 = 1.0000$

$R_{max} = 1.0000$

$K_1 = 1.0000$

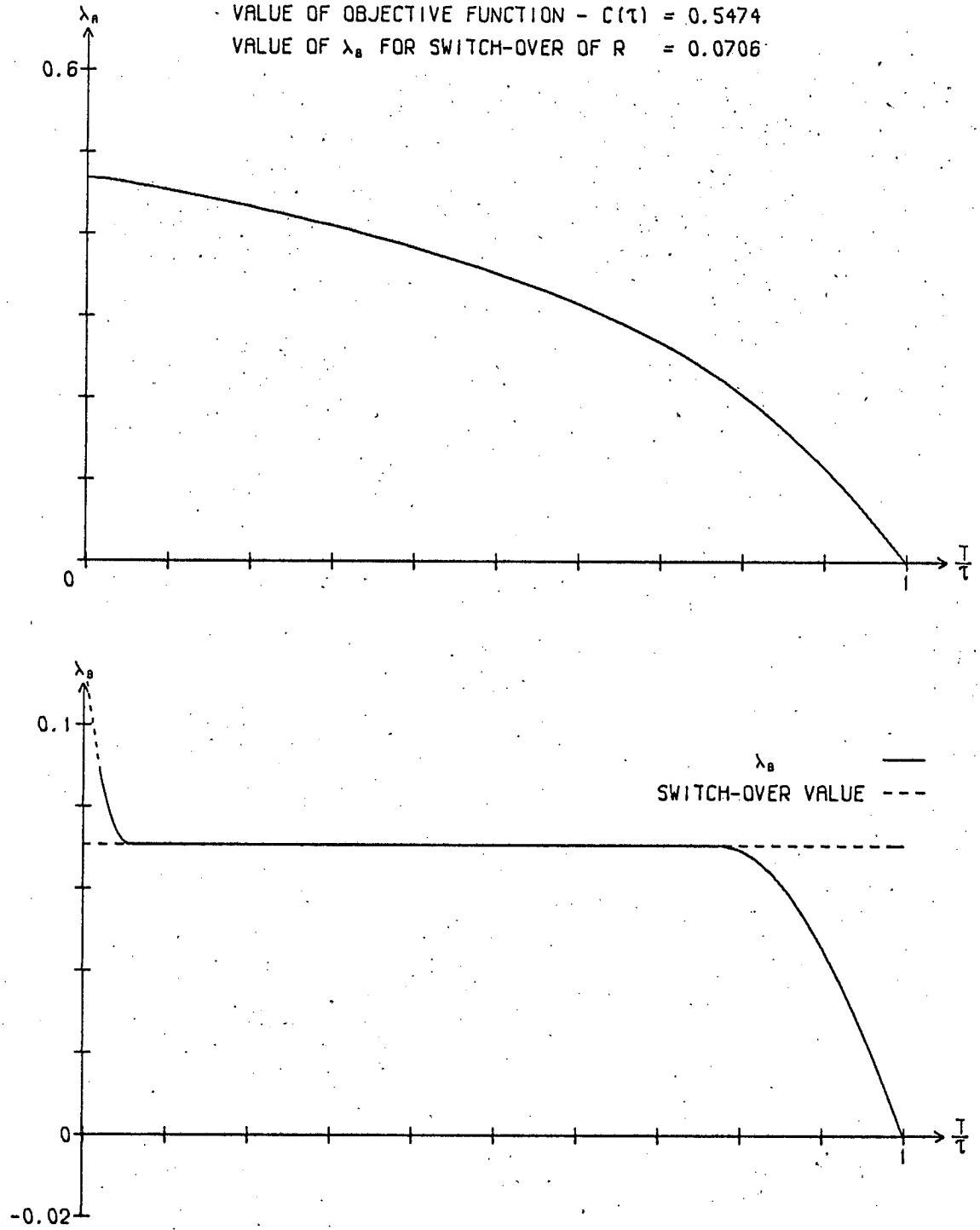
$K_2 = 2.0000$

$Q = 1.5000$

$\tau = 3.9999$

VALUE OF OBJECTIVE FUNCTION - $C(\tau) = 0.5474$

VALUE OF λ_B FOR SWITCH-OVER OF R = 0.0706

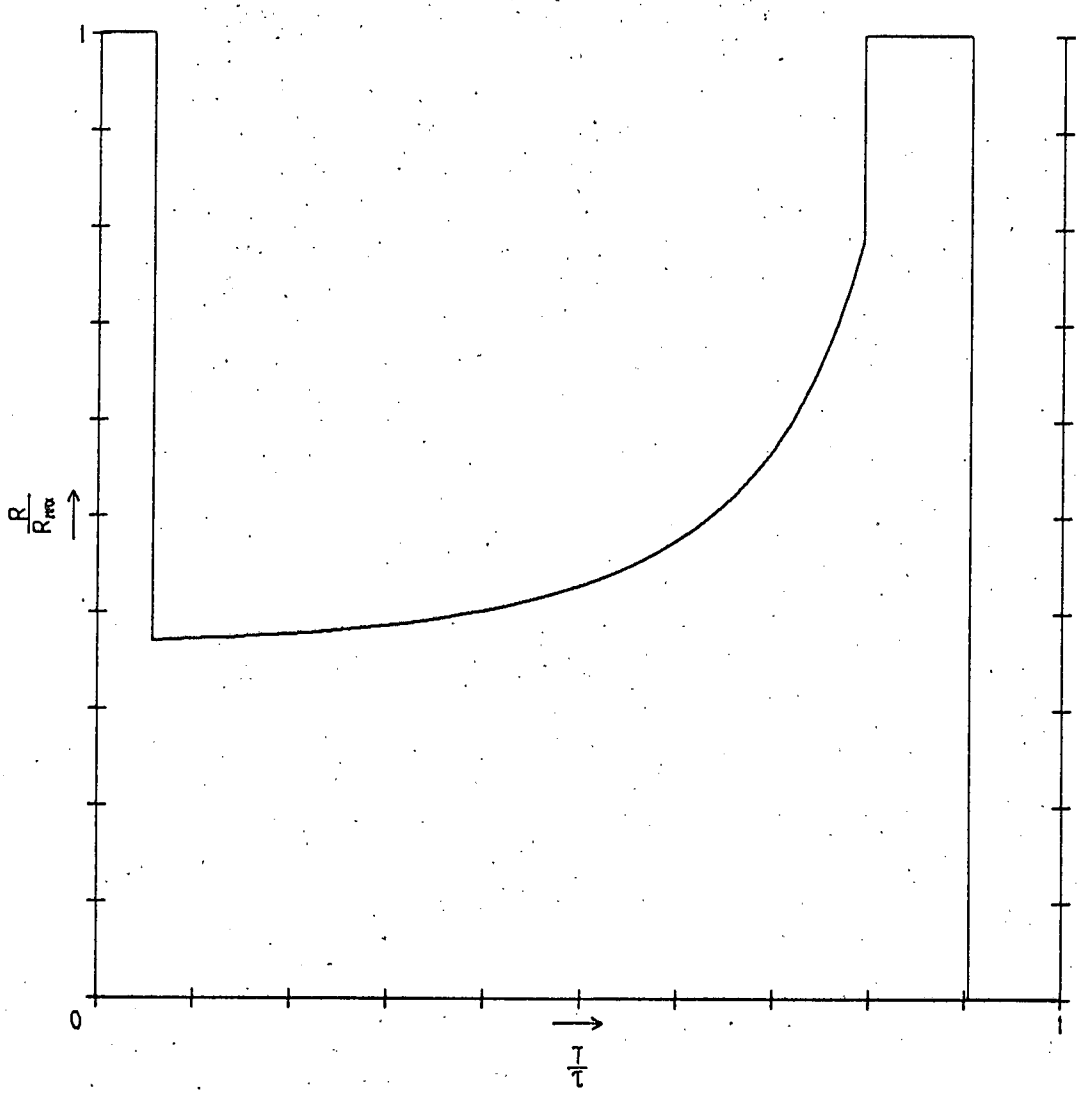


Graph 4.3

Adjoint variables for the control policy of Graph 4.1

A_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.9992
τ = 3.9998

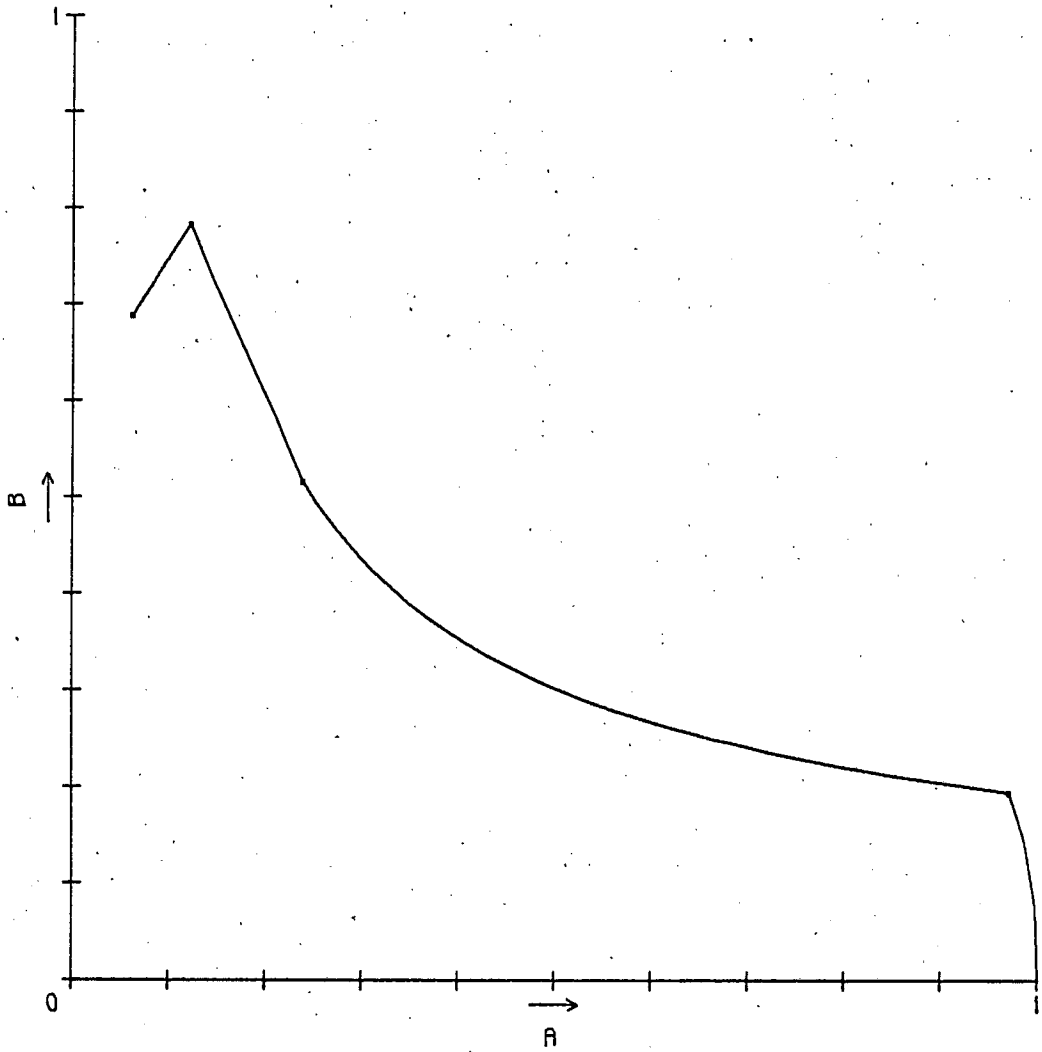
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5656



Graph 4.4

Control policy for Q specified and r constrained.
The value of Q is nominally 2.0

A_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.9992
τ = 3.9998
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5656

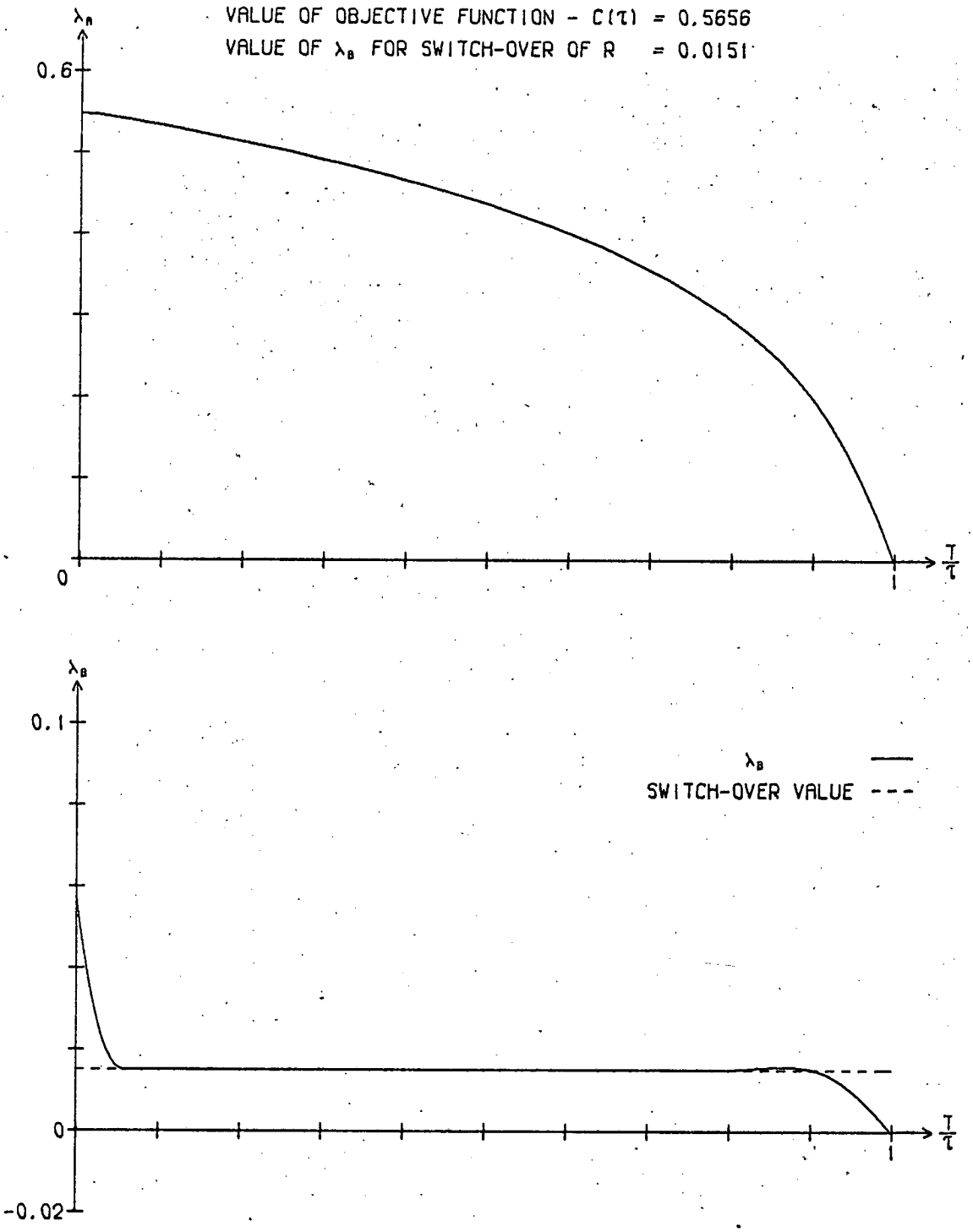


Graph 4.5

Solution trajectory in the a-b plane for the control policy of Graph 4.4

R_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.9992
τ = 3.9998

VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5656
VALUE OF λ_B FOR SWITCH-OVER OF R = 0.0151

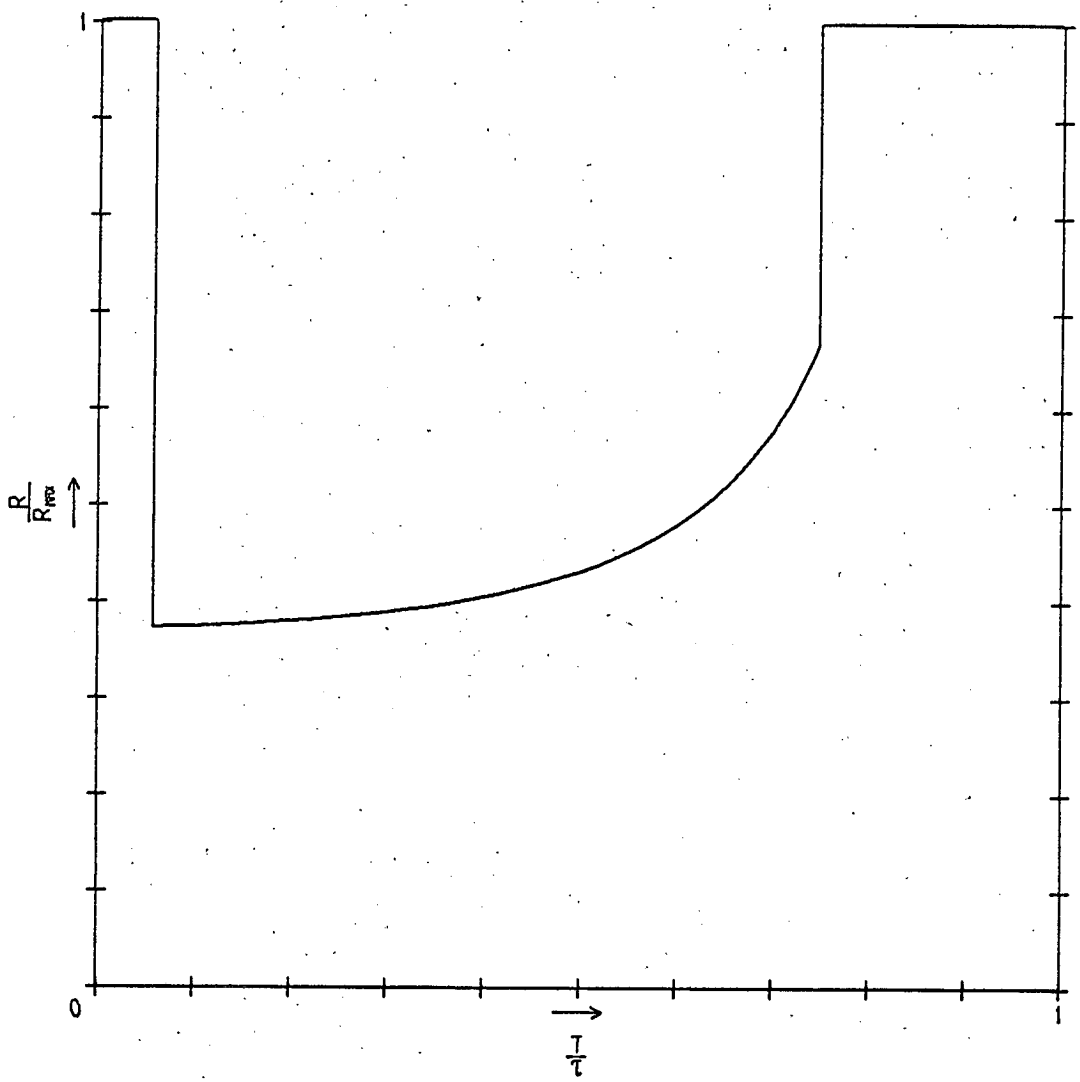


Graph 4.6

Adjoint variables for the control policy of Graph 4.4

A_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4380
τ = 3.9996

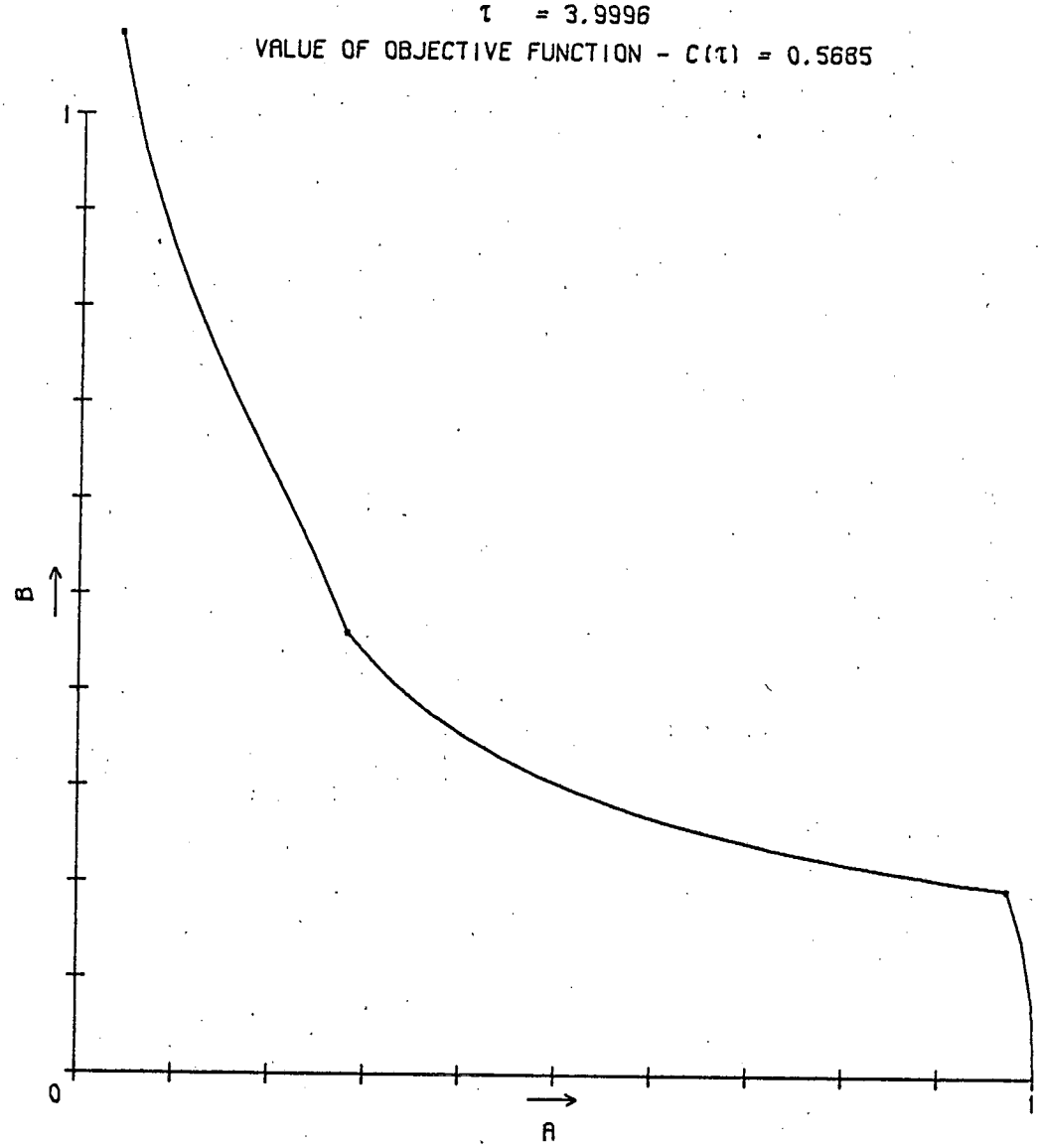
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5685



Graph 4.7

Control policy for Q unspecified

A_0 = 1.0000
R_{MAX} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4380
τ = 3.9996
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5685

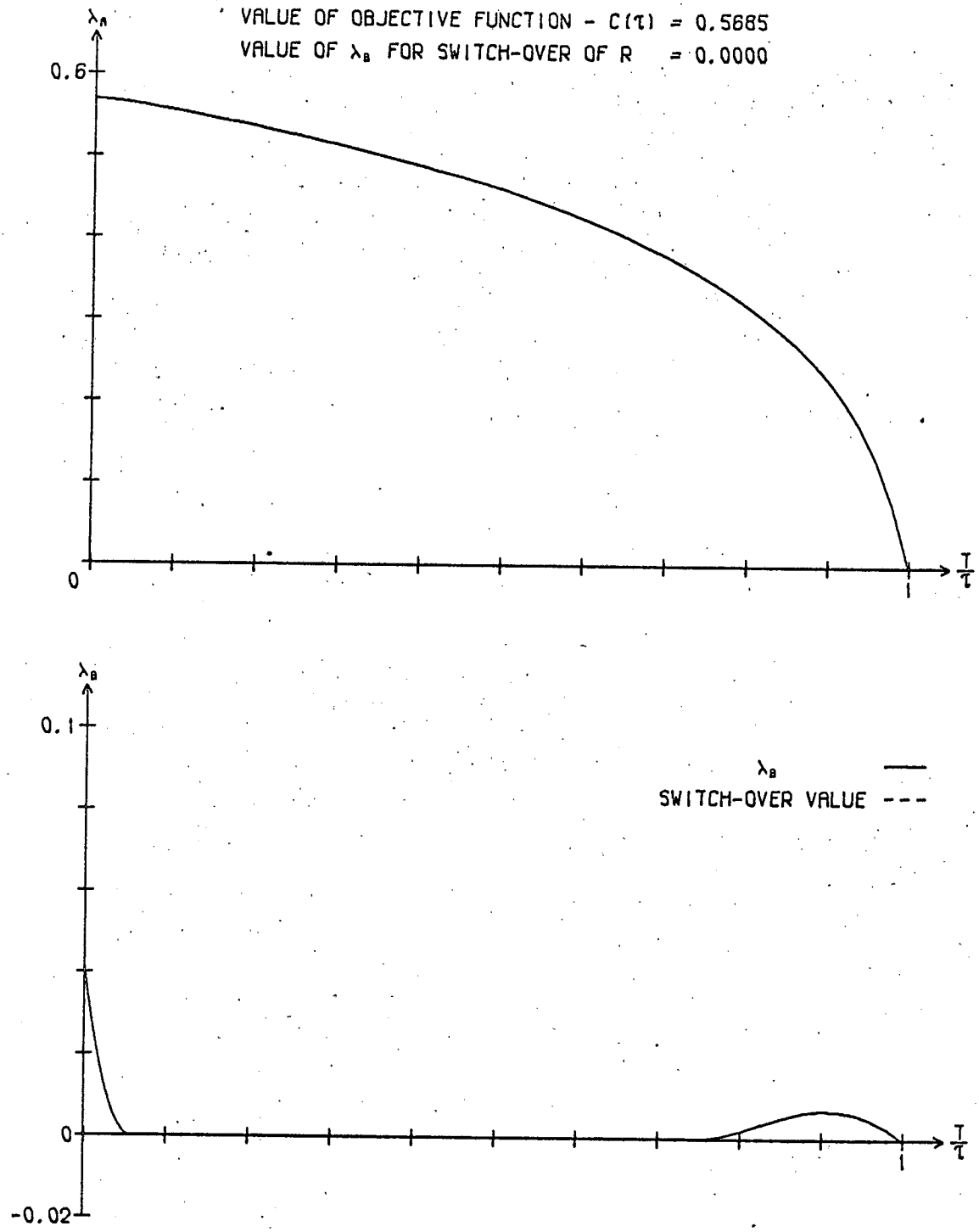


Graph 4.8

Solution trajectory in the a-b plane for the control policy of Graph 4.7

A_0 = 1.0000
R_{MAX} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4380
τ = 3.9996

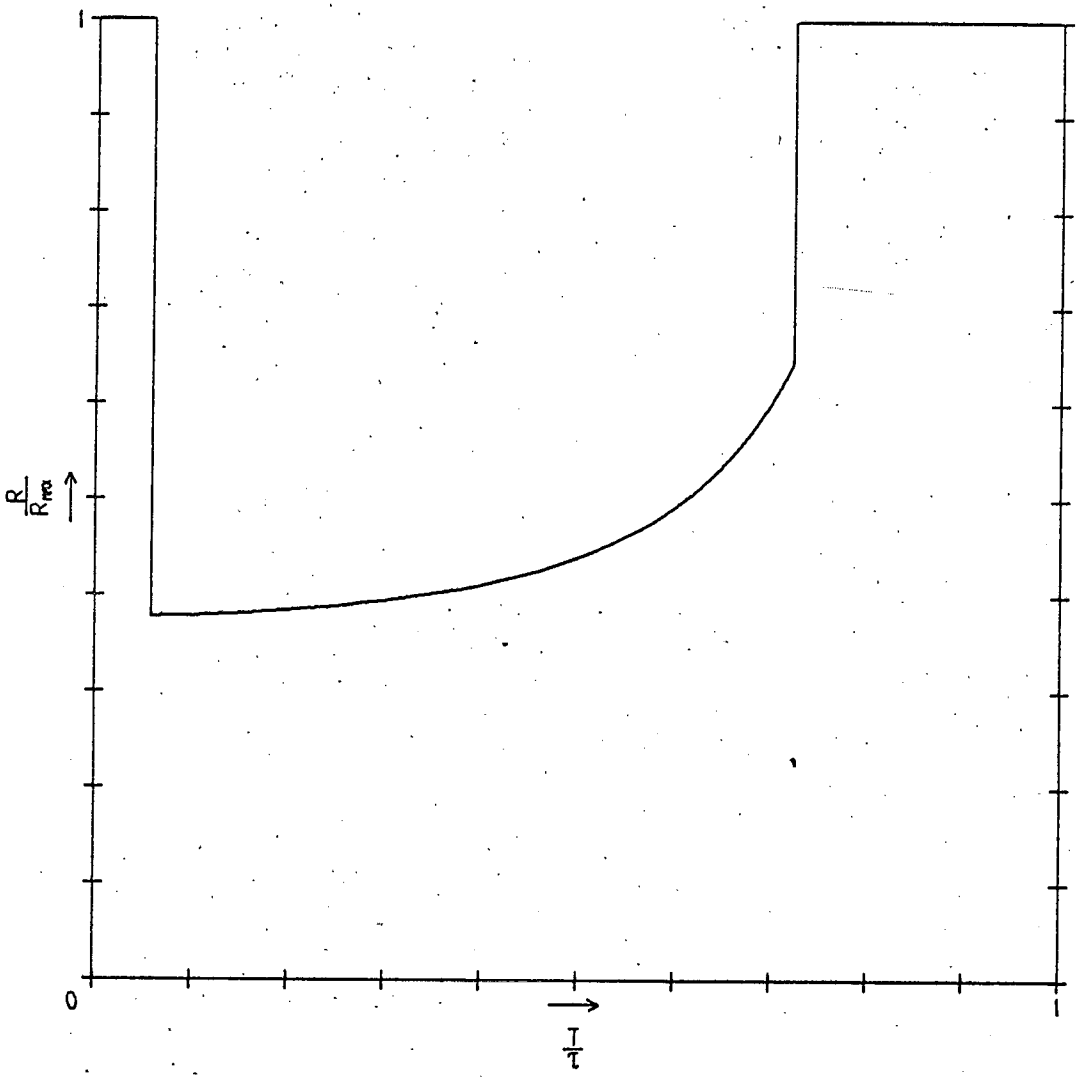
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5685
VALUE OF λ_B FOR SWITCH-OVER OF R = 0.0000



Graph 4.9

Adjoint variables for the control policy of Graph 4.7

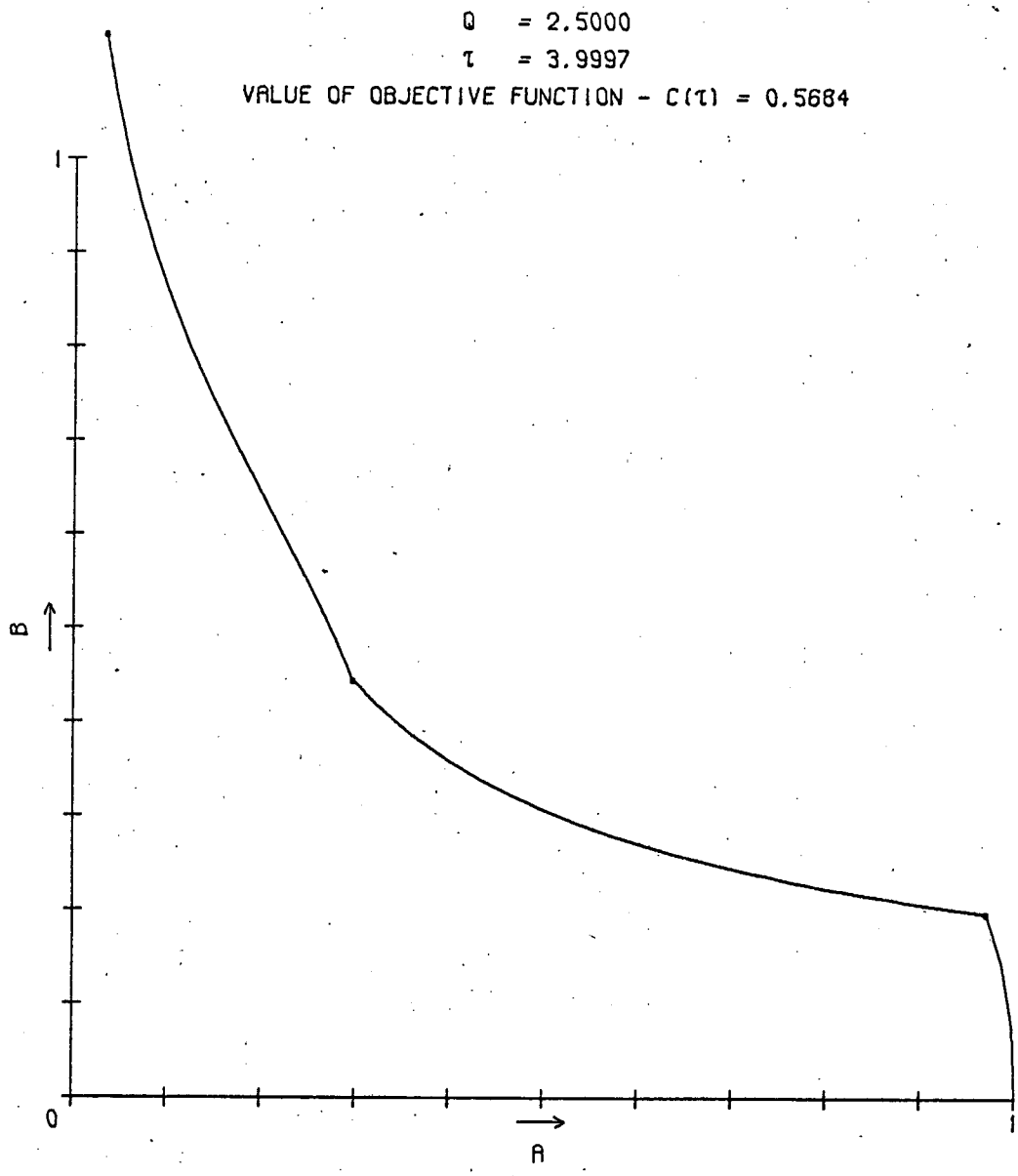
A_0 = 1.0000
R_{MAX} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.5000
τ = 3.9997
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5684



Graph 4.10

Control policy for Q specified and r constrained.
The value of Q is nominally 2.5

A_0 = 1.0000
R_{MAX} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.5000
τ = 3.9997
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5684

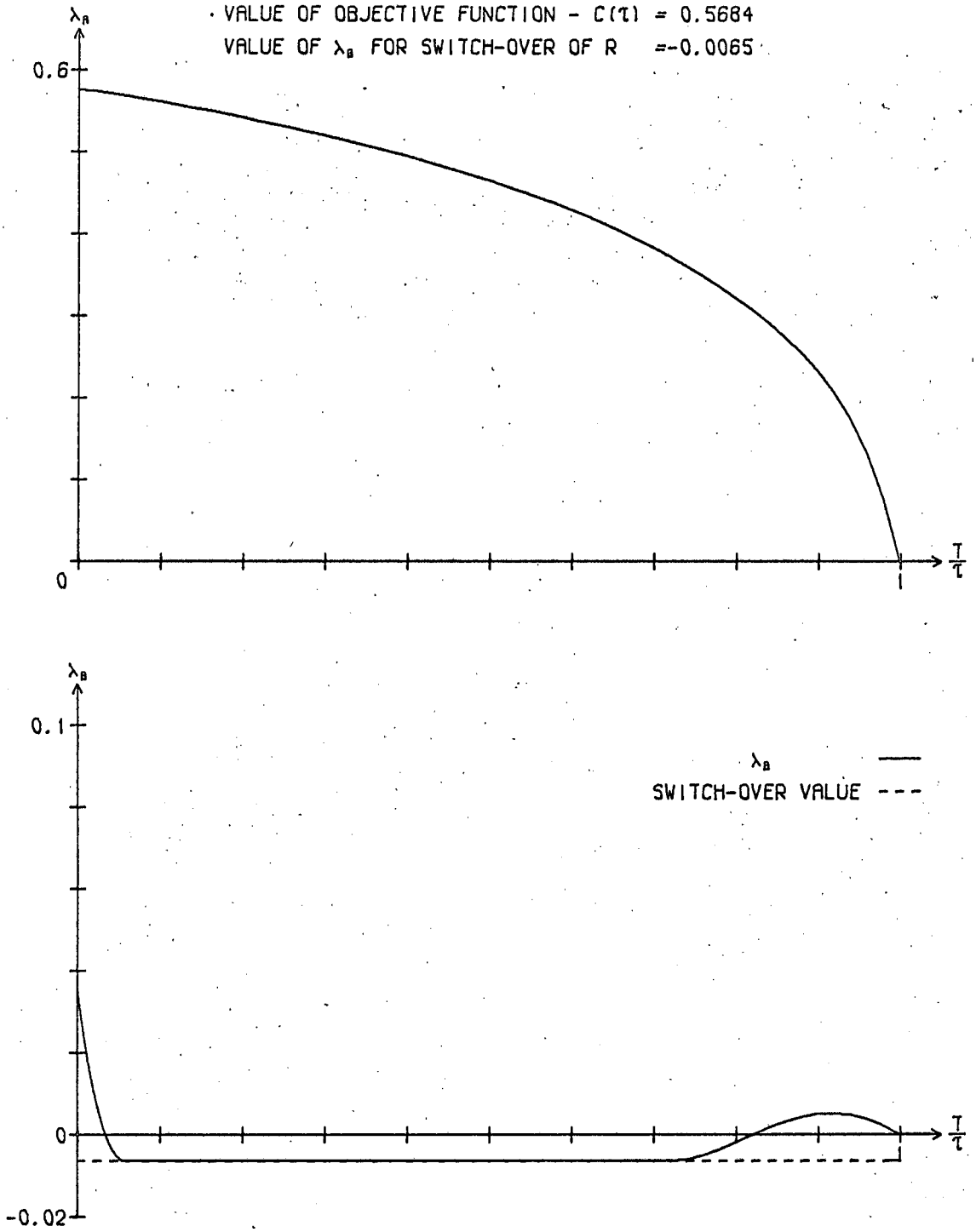


Graph 4.11

Solution trajectory in the a-b plane for the control policy of Graph 4.10

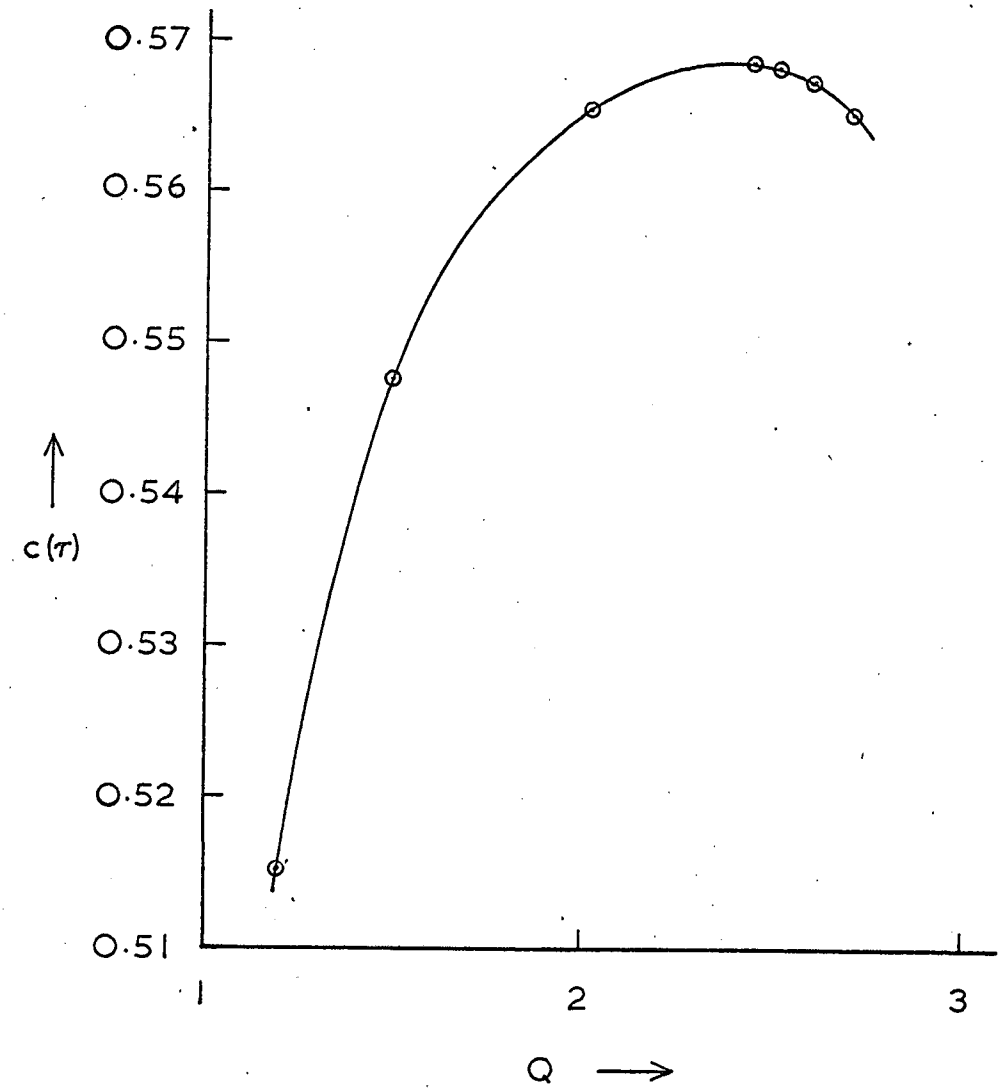
A_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.5000
τ = 3.9997

VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5684
VALUE OF λ_B FOR SWITCH-OVER OF R =-0.0065



Graph 4.12

Adjoint variables for the control policy of Graph 4.10



Graph 4.13

Final concentration of C for specified values of Q_o

$a_o = 1$, $k_1 = 1$, $k_2 = 2$, $r_{max} = 1$, and batch time $\tau = 4$.

Table 4.1

Summary of results from calculations of trajectories for different values of Q. $a_o = 1$, $k_1 = 1$, $k_2 = 2$, $r_{max} = 1$ and batch time $\tau = 4$. The values of the batch time and of Q are nominal.

Q	N	γ	$c(\tau)$
1.2	0.04356	-0.14865	0.5155
1.5	0.04423	-0.07058	0.5474
2.0	0.04205	-0.01508	0.5656
2.438	0.04162	0.00000	0.5685
2.5	0.03540	0.00649	0.5684
2.6	0.02635	0.01616	0.5674
2.7	0.01865	0.02470	0.5653

as expected, and the trajectories end with $r = 0$. When $\gamma > 0$, the final segment ends with $r = r_{max}$, and Graphs 4.10 to 4.12 for $Q = 2.5$ show that the final segment is $r = r_{max}$ throughout. Calculations for larger values of Q indicate that this form of the final segment is general, and no bang-bang switching can occur when $\gamma > 0$. Graphs 4.7 to 4.9 show the trajectory for Q unspecified, and are included for comparison.

It can be seen from these graphs that the shapes of the singular segments are very similar. They are not, however, identical since equation (4.13) for the singular segment in the a - b plane depends on N and γ, and these are different for different values of Q with the same batch time (see Table 4.1 above). A more rigorous proof of the difference is given in Appendix I.

It has already been mentioned in Chapter 3 that the value of the objective function should be greatest when there are least constraints on the control variable if imposing these constraints alters the shape of the control profile. Therefore it would be expected that the value of $c(\tau)$ will be greatest when Q is unspecified (for which $\gamma = 0$). Table 4.1 summarises the results of calculations for a range of values of Q, and the value of the objective function vs. Q is plotted in Graph 4.13. It is seen that the expected maximum is obtained, and the value of Q which arises when $\gamma = 0$ is therefore optimal for these values of r_{max} and τ.

Verification that the trajectories for different values of Q, obtained in the manner described, are optimal could be verified by a Gradients in Function Space search, as was done for Q unspecified in Chapter 3. However, since the profiles are of similar forms, and since Graph 4.13 of the objective function against Q is smooth, it is likely that they are optimal trajectories.

4.2 Specifying the Total Amount of Reactant B Added, With No Constraint on r

It is seen from the results of Graphs 4.1 to 4.3 that when the amount of B which is specified is rather less than the amount required when no such specification is made, the final non-singular segment is a "coasting" segment, with no addition of reactant, which starts from a point on the singular segment where r is less than its maximum value. If no constraint is imposed on the rate of addition, then it was seen in

Chapter 3 that the total amount of B consumed is in theory infinite. Any specification of the amount of B to be added if r is unconstrained will therefore be considerably less than this amount, and logically the $\overset{\text{final}}{\wedge}$ segment of the control policy should again be a coasting segment, leaving the singular segment at a point where r is finite. The only region where r is at its limiting value in Graph 4.1 is at the beginning of the batch, to build up a sufficient concentration of B to initiate the singular segment, and this part of the control profile would be eliminated when there is no constraint on r by allowing a specified initial concentration of B in the reactor. It is therefore not strictly necessary to impose an upper limit on r to model a practical reactor, and the removal of this limit will then enable a maximum performance figure to be calculated which can be used as a standard for comparison of reactors in which there is a practical limit on the maximum rate of addition of a reactant.

4.2.1 Theoretical Considerations

Equation (4.13), which is the equation for the singular segment in the a - b plane, can be rearranged to give

$$N = \frac{k_2\, ab^2(1 - \gamma)}{k_1 + 2k_2 b} - \frac{\gamma r_{max}\ \text{sgn}\ 1(\gamma)}{k_1} . \qquad (4.15)$$

Now let $r_{max} \to \infty$. The first term on the right hand side of equation (4.15) remains finite, and, in order that the second term also remains finite, then either $\gamma \leqslant 0$ for all $r_{max} \to \infty$ (in which case this second term is zero

for all $r_{max} \to \infty$), or $\gamma \to 0$ from above in such a way that γr_{max} remains finite ($\gamma \to 0$ from above implies that sgn $1(\gamma)$ remains at unity).

It has already been shown earlier in this chapter that, if $\gamma \geq 0$, the final segment must end with $r = r_{max}$ (equation (4.5)). In the limit of $r_{max} \to \infty$, this becomes an instantaneous addition of a quantity of B at $t = \tau$, and if Q is specified this amount of B must be finite. It is readily shown that such instantaneous addition of B cannot satisfy the maximum principle.

At $t = \tau$, the Hamiltonian is given by equation (4.4)

$$H_\tau = \gamma r + k_1 a(\tau) b(\tau) \text{ where } \gamma r > 0.$$

At a point immediately before this instantaneous addition of B, $r = 0$, $a = a(\tau)$, $b = b(\tau) - \delta q$ (where δq is the quantity of B added at $t = \tau$), $\lambda_a = \lambda_b = 0$, $\lambda_c = 1$ (since instantaneous addition of B causes a step discontinuity in only the differentials of the adjoint variables). The value of the Hamiltonian at this point before the addition of B is therefore

$$H = k_1 a(\tau) \{b(\tau) - \delta q\} + \gamma r$$

which cannot be equal to H_τ unless $\delta q = 0$. Thus instantaneous addition of a quantity of B at $t = \tau$ violates the maximum principle. It follows therefore that γ must be less than zero for $r_{max} \to \infty$.

For γ less than zero, equation (4.15) for the singular segment in the a - b plane becomes

$$N = \frac{k_2 ab^2(1 - \gamma)}{k_1 + 2k_2 b}. \qquad (4.16)$$

This can intersect with the terminal hyperbola of equation (3.42) in $a, b > 0$ only if $\gamma < -1$. It has already been shown that for $\gamma < -1$ the "optimal control" is no reaction. The relative positions of the terminal hyperbola and the singular segment must therefore be as shown in curves A and B respectively of Graph 3.4, and a trajectory which satisfies the maximum principle will probably therefore consist of

(1) instantaneous addition of a sufficient quantity of B to initiate the singular segment

(2) singular segment

(3) non-singular segment, consisting of $r = 0$ with possible instantaneous additions of finite quantities of B at different points.

By considering the limit of $r_{max} \to \infty$, it follows that instantaneous additions of quantities of B during this final segment can occur only when $\lambda_b = -\gamma (> 0)$, and can make physical sense only if λ_b decreases from $-\gamma$ after this addition (since $\lambda_b > -\gamma$ implies $r = r_{max}$ to satisfy the maximum principle). Such a point occurs at the beginning of this final segment, since $\lambda_b = -\gamma$ on the singular segment. It is shown later that instantaneous addition of a quantity of B at this point does not provide a valid solution trajectory as it does not cause λ_b to decrease from $-\gamma$. No further points of $\lambda_b = -\gamma$ have been found for any of the trial calculations made. From the arguments given at the introduction to this section it seems likely that such instantaneous additions do not form part of the solution trajectory, being, as they are, equivalent to bang-bang control for r constrained, and so the final segment

is probably a simple coasting segment.

The calculation procedure for the solution trajectory follows similar lines to that used when r was constrained. However, since in the final segment it is assumed that no B is added to the batch, some saving in computation can be made. For given values of N and γ, the initial concentration of B can be calculated from equation (4.16), and the control profile along the singular segment calculated in the usual fashion. However, instead of calculating the singular segment up to $r = r_{max}$, it is calculated until $q(t) = Q$, the specified quantity of B to be added during the reaction. This point is used as the departure point from the singular segment for integration of the final coasting segment. To obtain the condition of λ_a and λ_b both reaching zero simultaneously, instead of adjusting the departure point from the singular segment, γ is adjusted and the full trajectory of singular and non-singular segments recalculated. The value of N is then adjusted and the full procedure for calculating the solution profile repeated until the desired batch time is obtained.

4.2.2 Results of Calculations

Two series of calculations were made for Q specified, as in section 1 of this chapter, and values of r_{max} of 1, 2, 5 and 10, the values of the other reaction parameters and the batch time being as for previous calculations. The resulting profiles for $Q = 2.5$ are shown in Graphs 4.14 to 4.25, where it is seen that the form of the final non-singular segment is $r = r_{max}$ throughout for $r_{max} = 1$, becoming $r = r_{max}$

initially, switching to $r = 0$, for $r_{max} = 2$, and progressing to $r = 0$ throughout for $r_{max} = 5$ and $r_{max} = 10$. This progressive change is similar to that observed when r_{max} is constant and Q is reduced. It occurs simply as a result of a specified value of Q of 2.5 being greater than the optimal value of Q for $r_{max} = 1$, but as r_{max} is increased the optimal value of Q also increases, and the value 2.5 is progressively a smaller proportion of this optimal value of Q.

Following the progression of the shape of the control profile as r_{max} is increased, it is logical that when $r_{max} \to \infty$ the final segment should be a coasting segment with no instantaneous additions of quantities of B at any point during the segment. A calculation of such a trajectory for $Q = 2.5$ was made, and the resulting profiles are shown in Graphs 4.26 to 4.28, where it is seen that the expected form of the final segment does indeed satisfy the maximum principle. Furthermore, the value of the objective function for r unconstrained is larger than that obtained for all calculations of r constrained, with different values of r_{max}, which is what was expected, and this helps to confirm the optimality of this profile.

The results of the calculations for the various values of r_{max} for $Q = 2.5$ are summarised in Table 4.2. The lack of gradation in the values of N and γ results from the different forms of the final segments of the trajectories. The final concentration of C for these calculations is plotted against r_{max} in Graph 4.29, and it is seen that this curve approaches asymptotically the value of $c(\tau)$ for r unconstrained. The second similar series of calculations was made for $Q = 1.2$, and some of the resulting profiles for $r_{max} = 1$, 10 and unconstrained are

R_0 = 1.0000

R_{max} = 1.0000

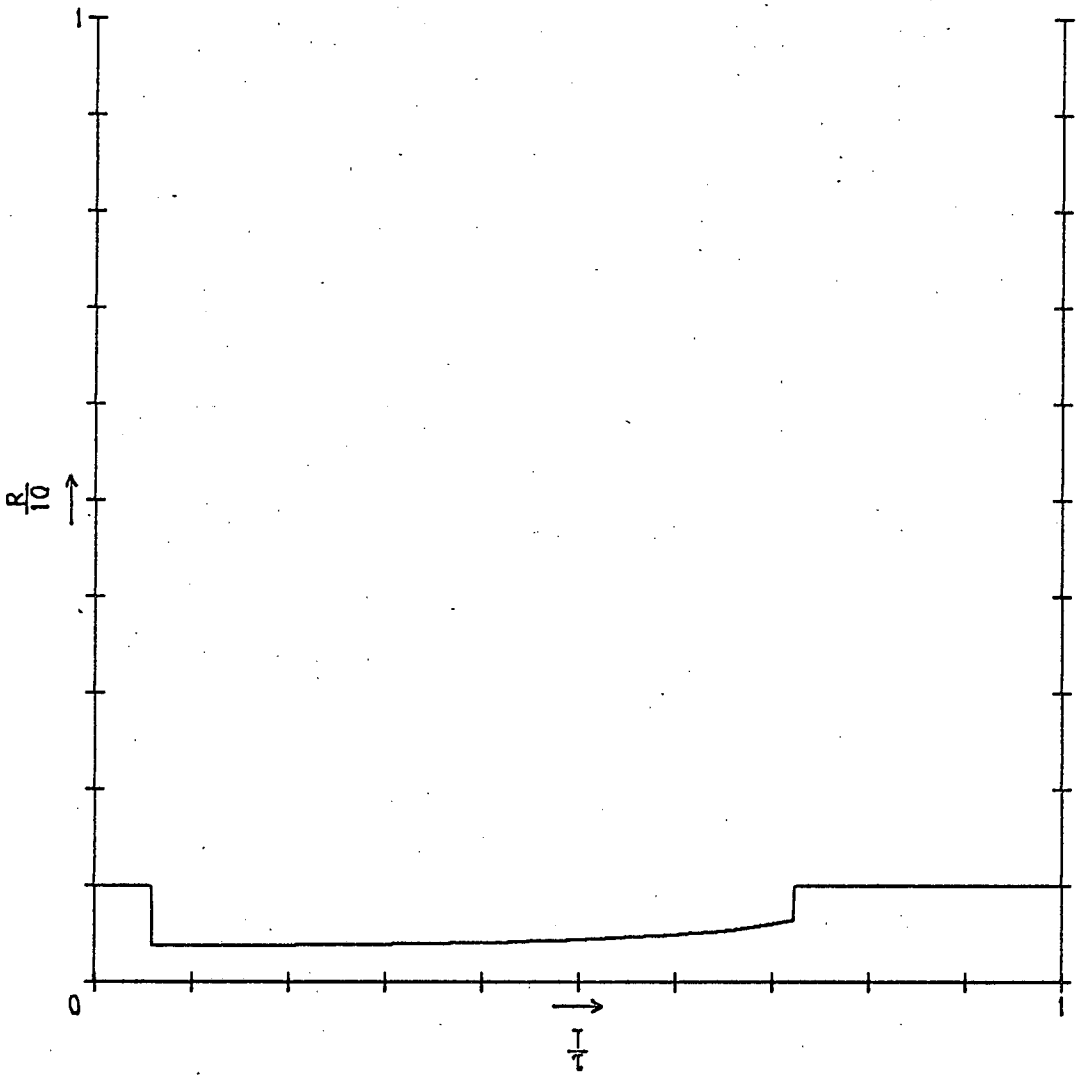
K_1 = 1.0000

K_2 = 2.0000

Q = 2.5000

τ = 3.9997

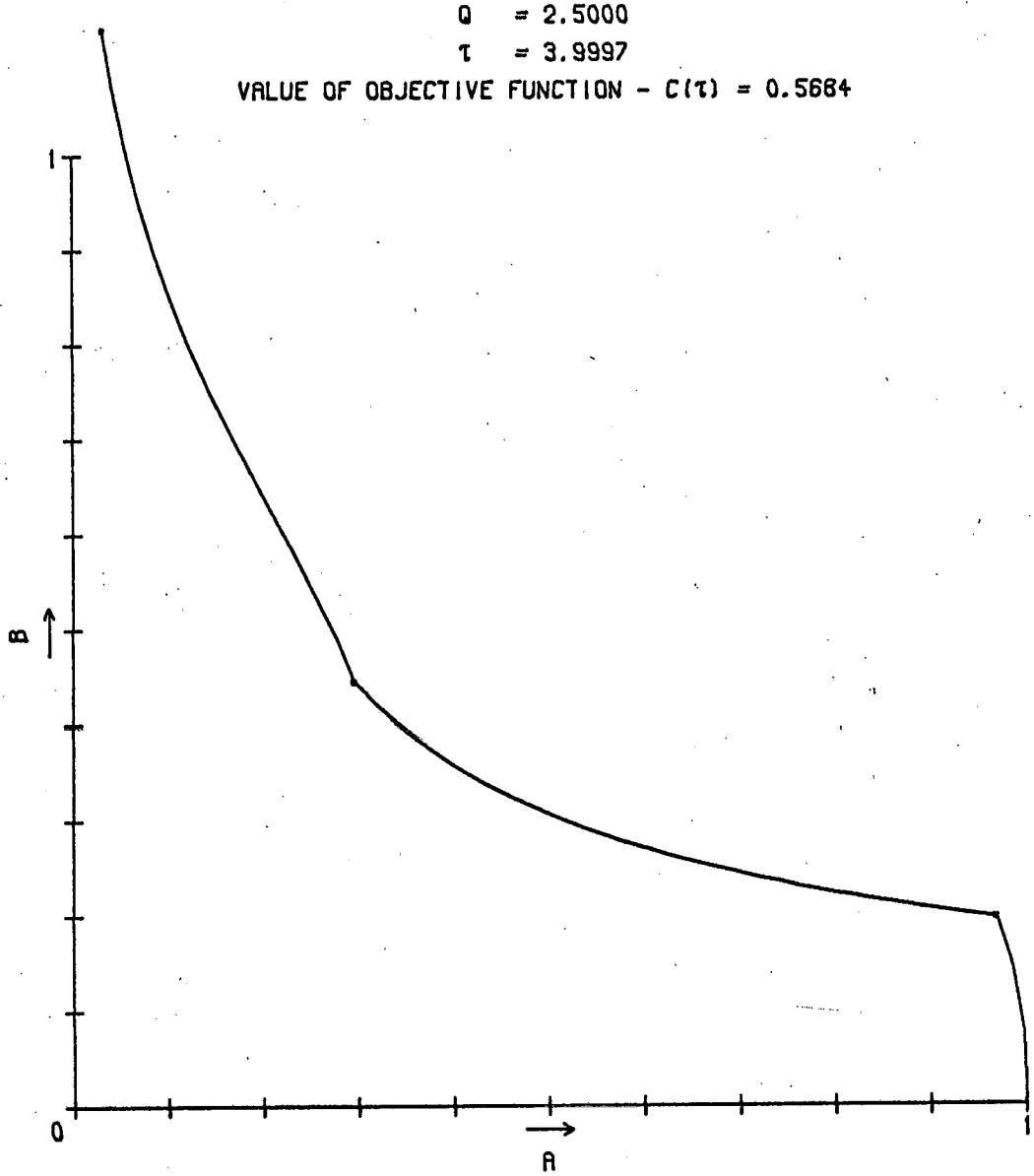
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5684



Graph 4.14

Control policy for Q = 2.5 and r_{max} = 1

A_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.5000
τ = 3.9997
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5684

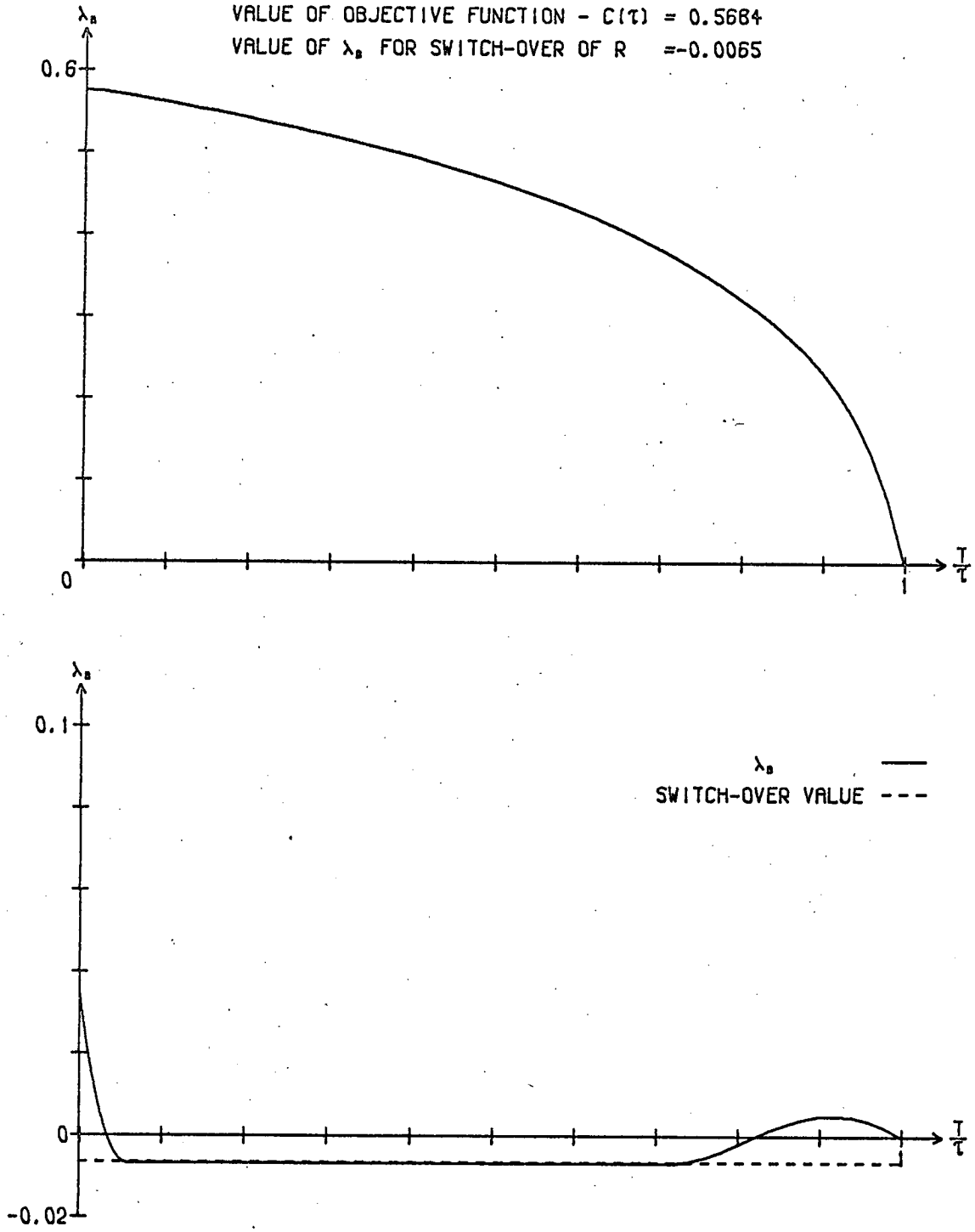


Graph 4.15

Solution trajectory in the a-b plane for the control policy of Graph 4.14

A_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.5000
τ = 3.9997

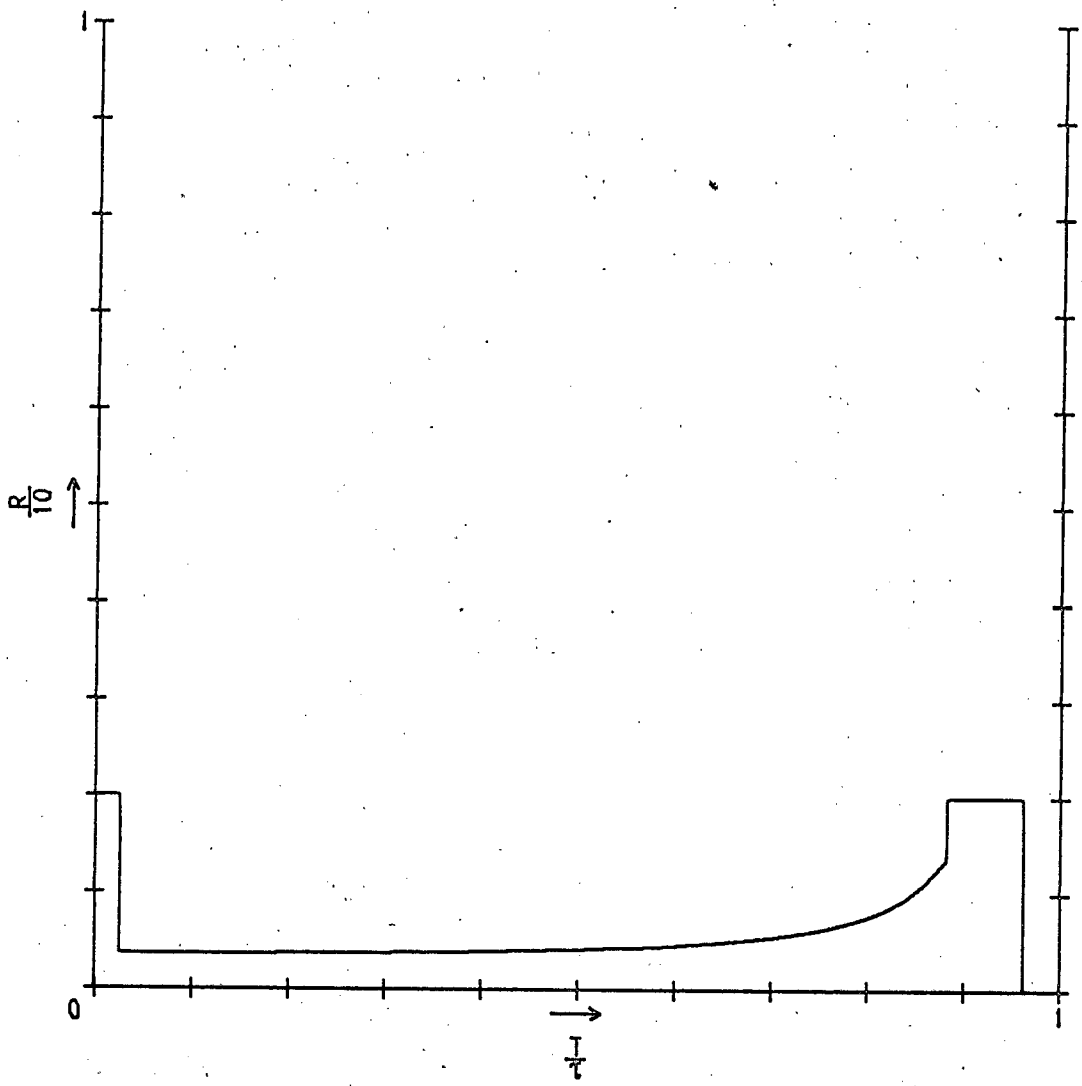
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5684
VALUE OF λ_B FOR SWITCH-OVER OF R =-0.0065



Graph 4.16

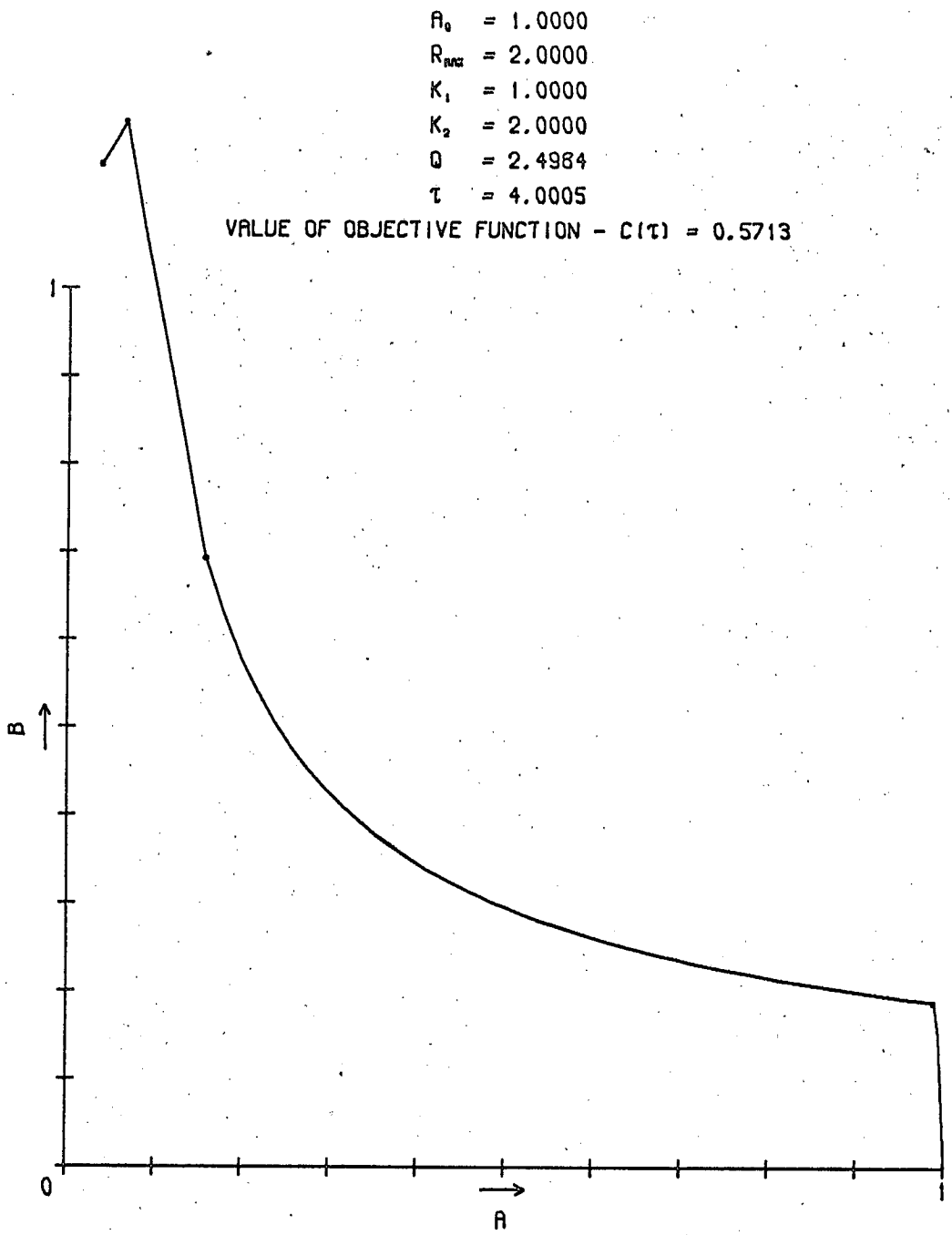
Adjoint variables for the control policy of Graph 4.14

A_0 = 1.0000
R_{max} = 2.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4984
τ = 4.0005
VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.5713



Graph 4.17

Control policy for Q = 2.5 and r_{max} = 2

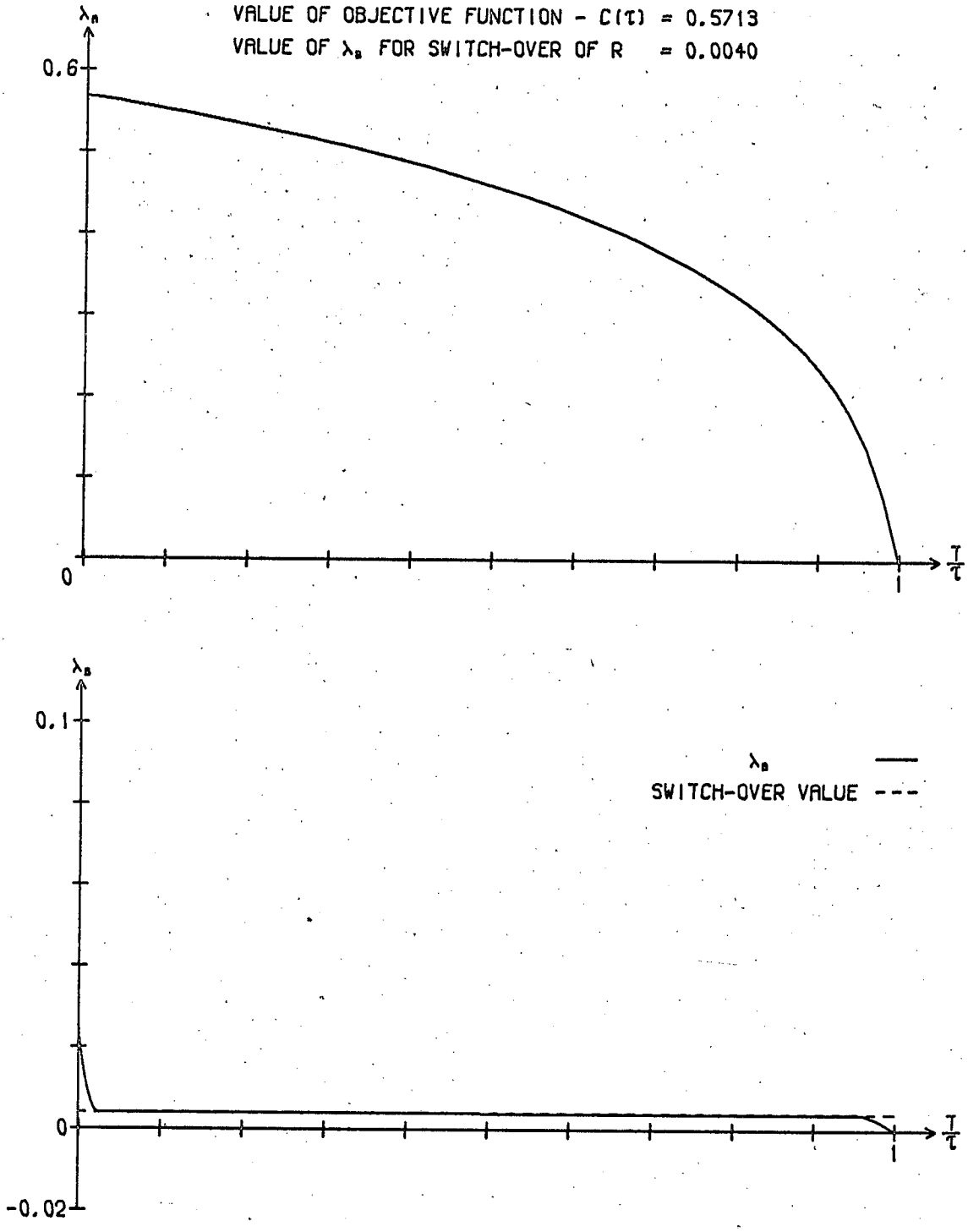


Graph 4.18

Solution trajectory in the a-b plane for the control policy of Graph 4.17

A_0 = 1.0000
R_{max} = 2.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4984
τ = 4.0005

VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5713
VALUE OF λ_a FOR SWITCH-OVER OF R = 0.0040

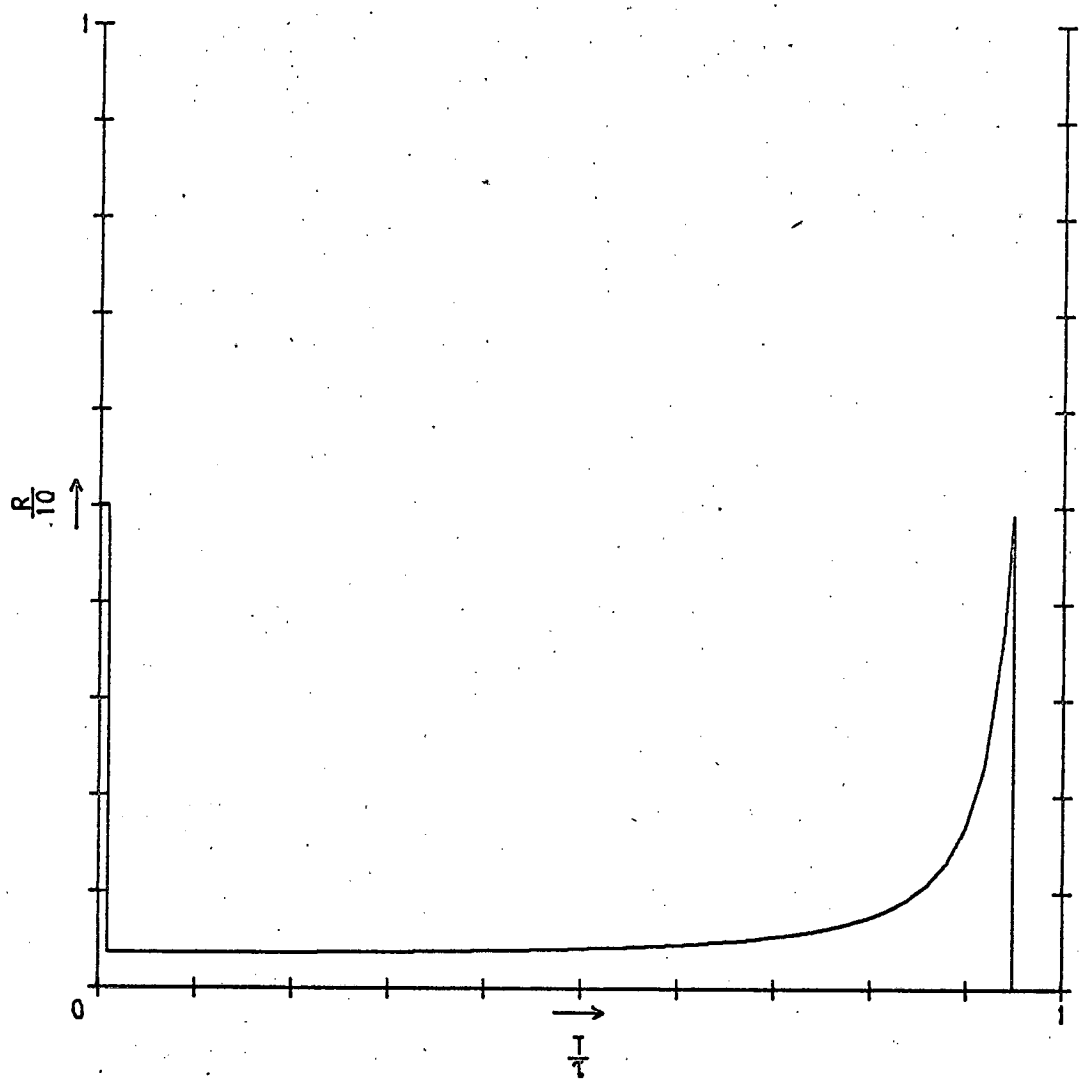


Graph 4.19

Adjoint variables for the control policy of Graph 4.17

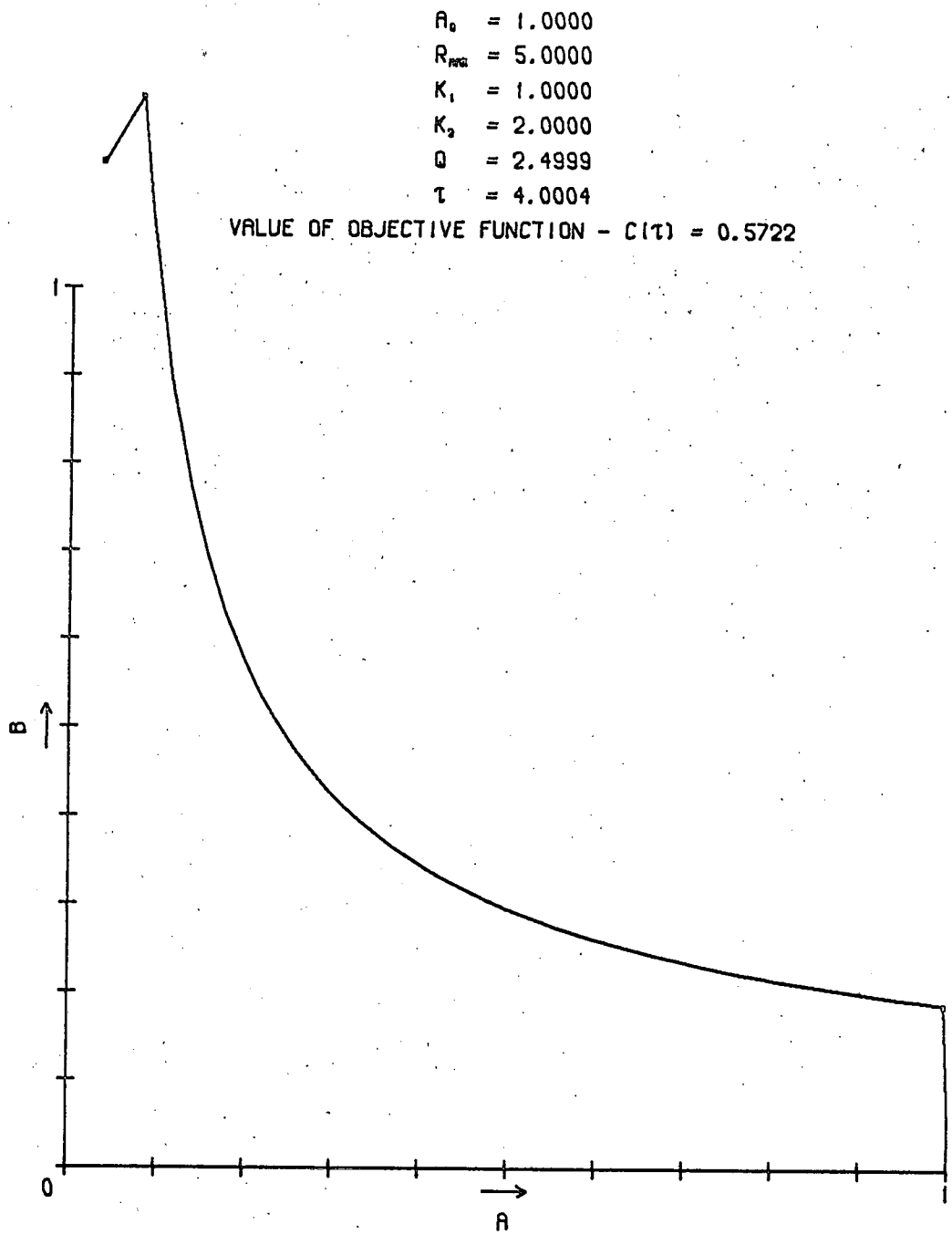
A_0 = 1.0000
R_{max} = 5.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4999
τ = 4.0004

VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5722



Graph 4.20

Control policy for Q = 2.5 and r_{max} = 5

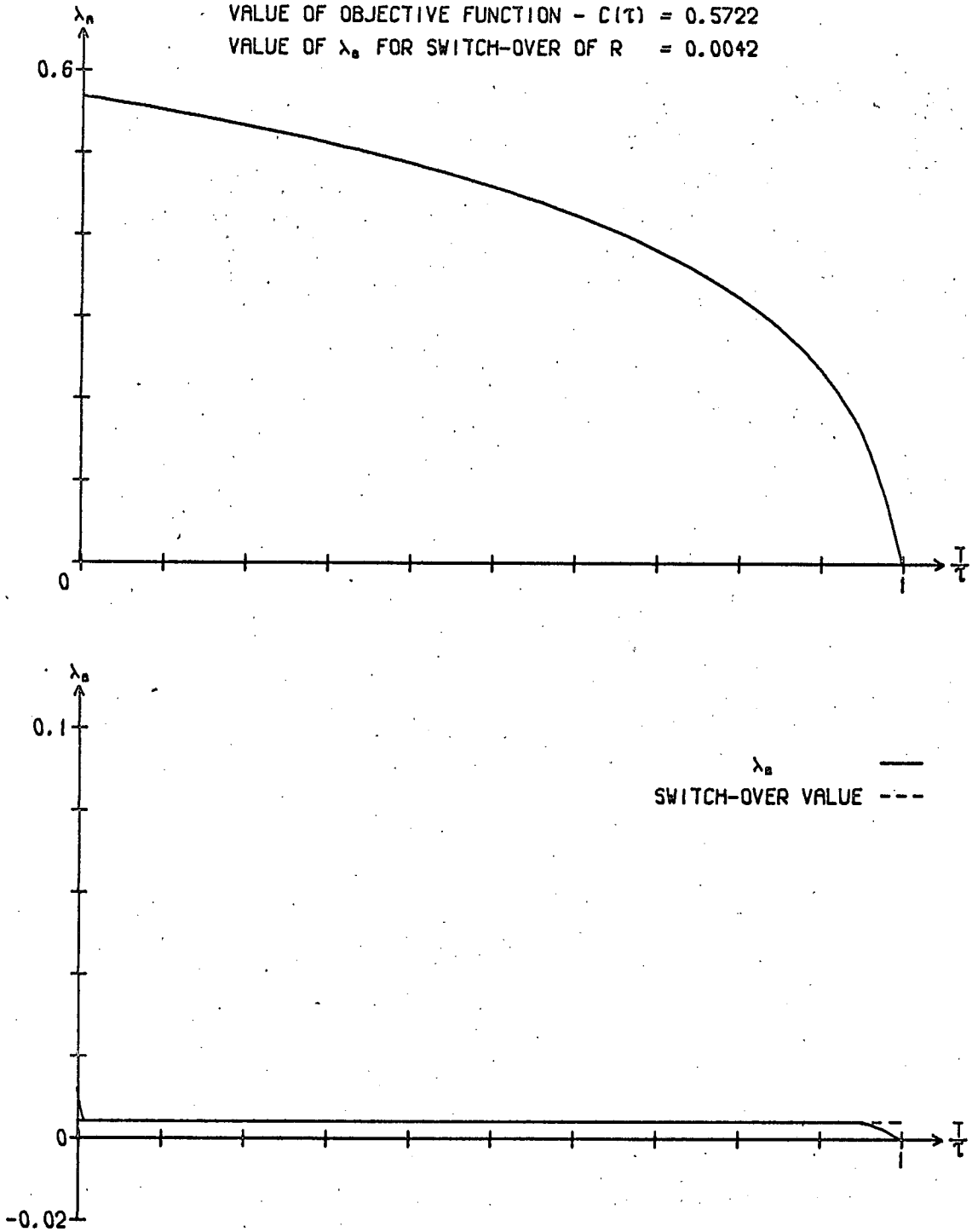


Graph 4.21

Solution trajectory in the a-b plane for the control policy of Graph 4.20

A_0 = 1.0000
R_{max} = 5.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4999
τ = 4.0004

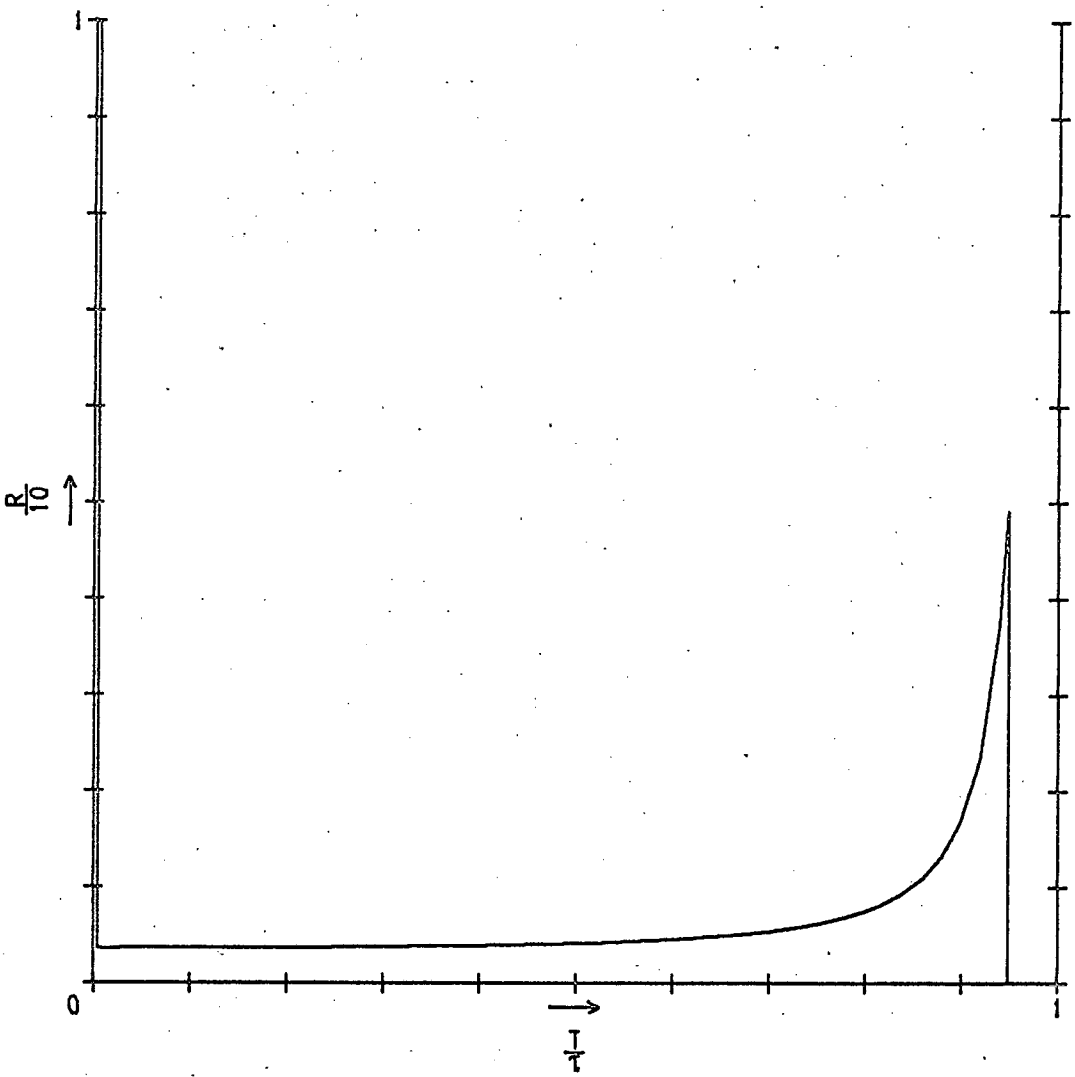
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5722
VALUE OF λ_a FOR SWITCH-OVER OF R = 0.0042



Graph 4.22

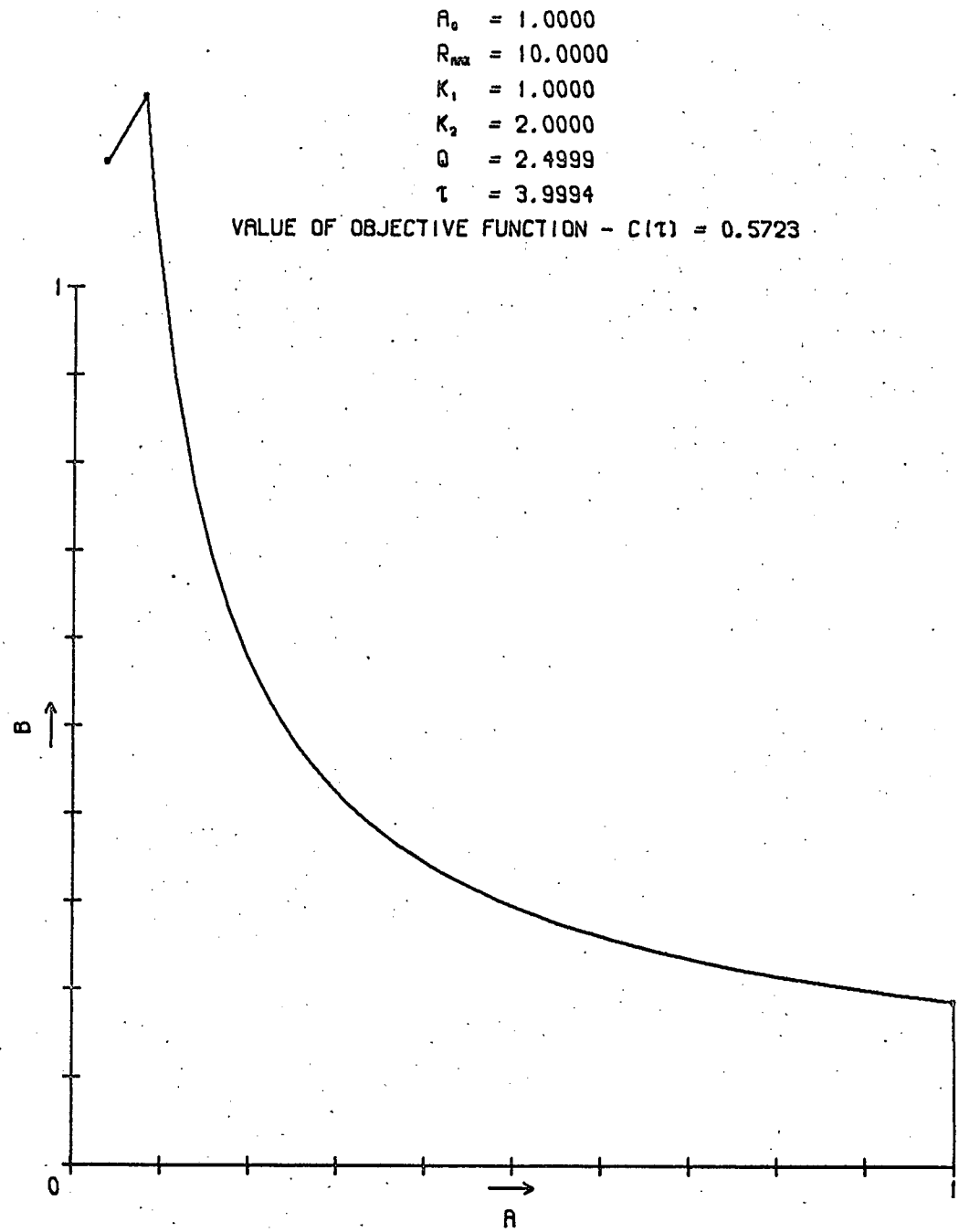
Adjoint variables for the control policy of Graph 4.20

R_0 = 1.0000
R_{max} = 10.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4999
τ = 3.9994
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5723



Graph 4.23

Control policy for Q = 2.5 and r_{max} = 10

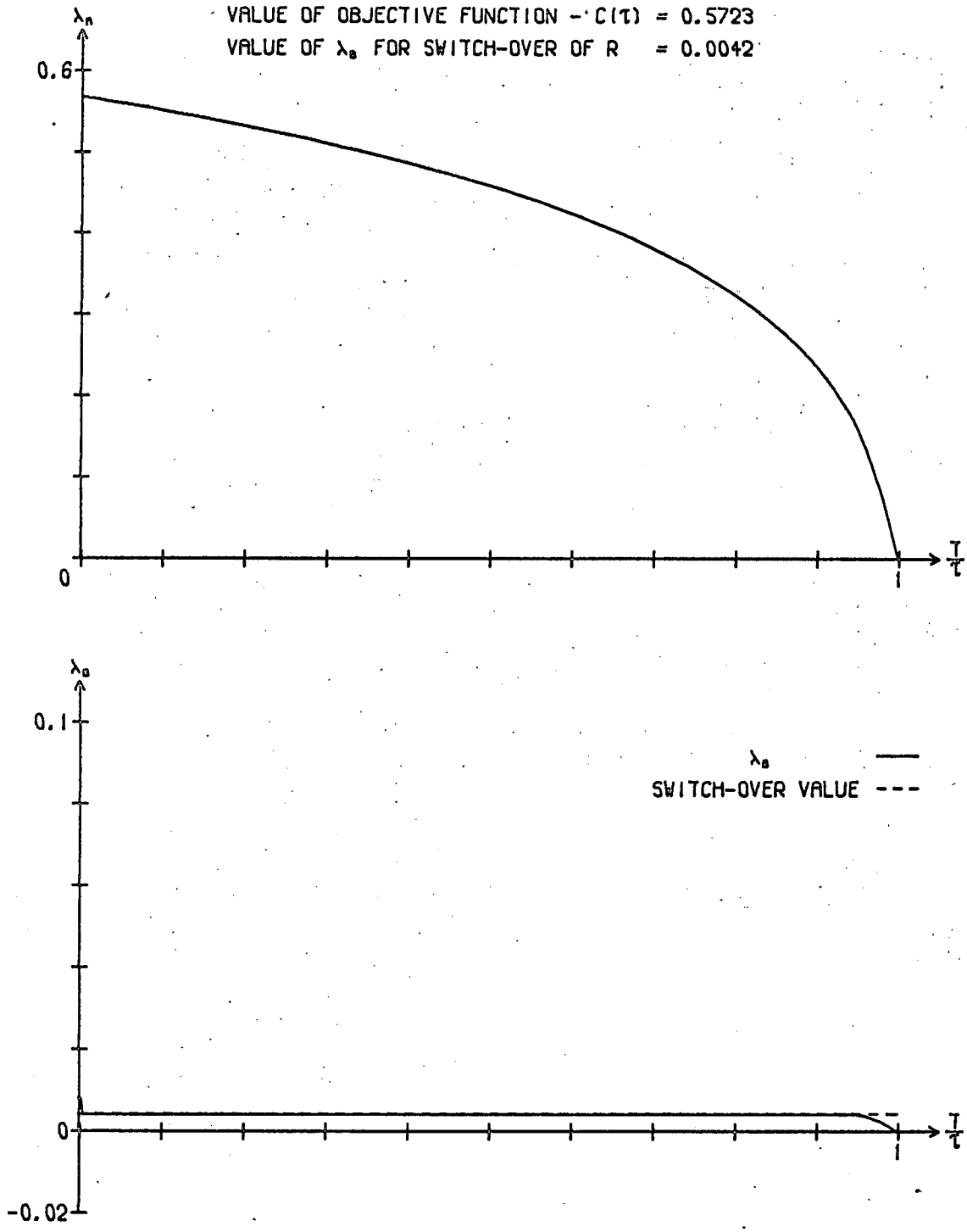


Graph 4.24

Solution trajectory in the a-b plane for the control policy of Graph 4.23

A_0 = 1.0000
R_{max} = 10.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.4999
τ = 3.9994

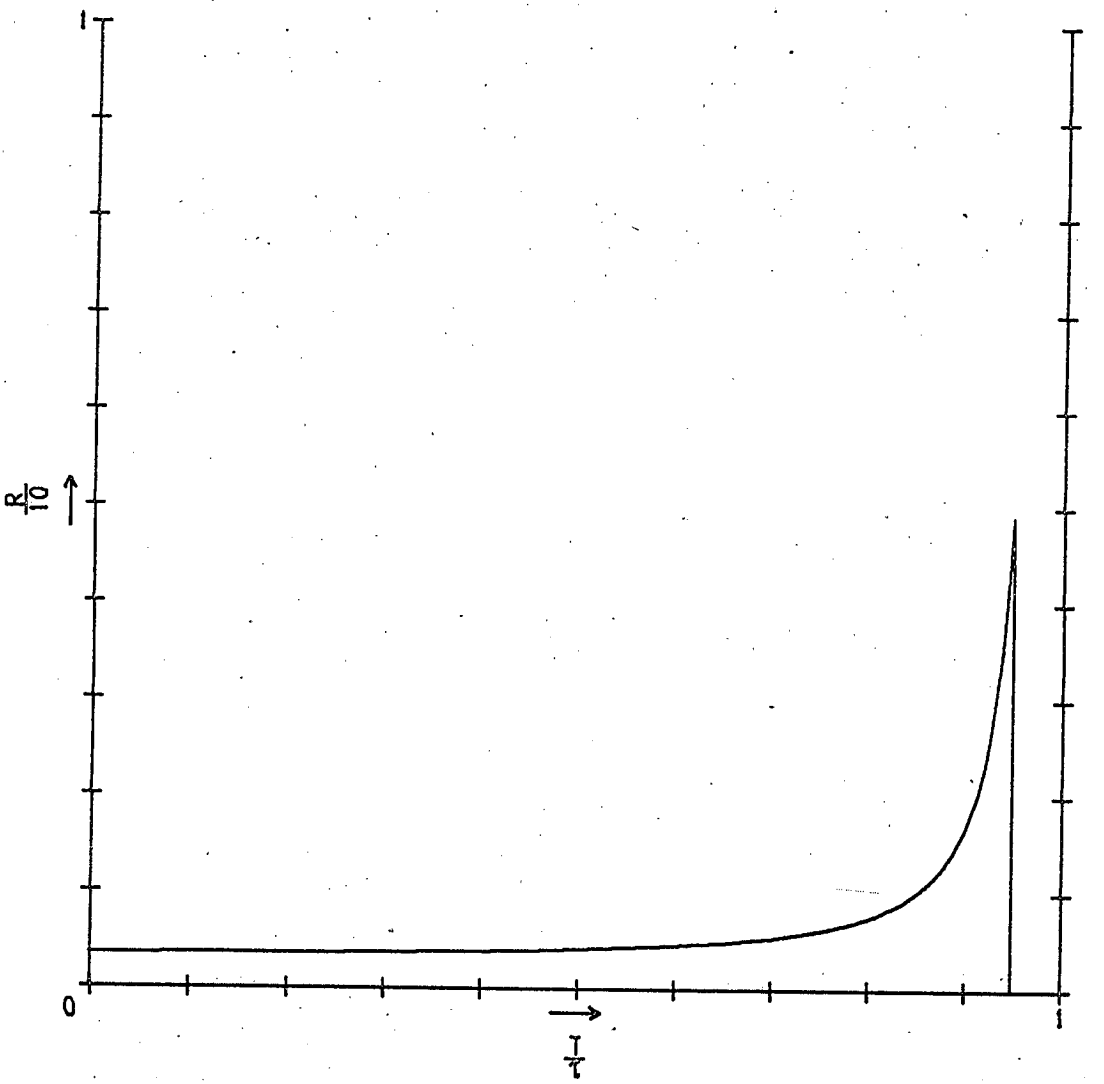
VALUE OF OBJECTIVE FUNCTION -C(τ) = 0.5723
VALUE OF λ_a FOR SWITCH-OVER OF R = 0.0042



Graph 4.25

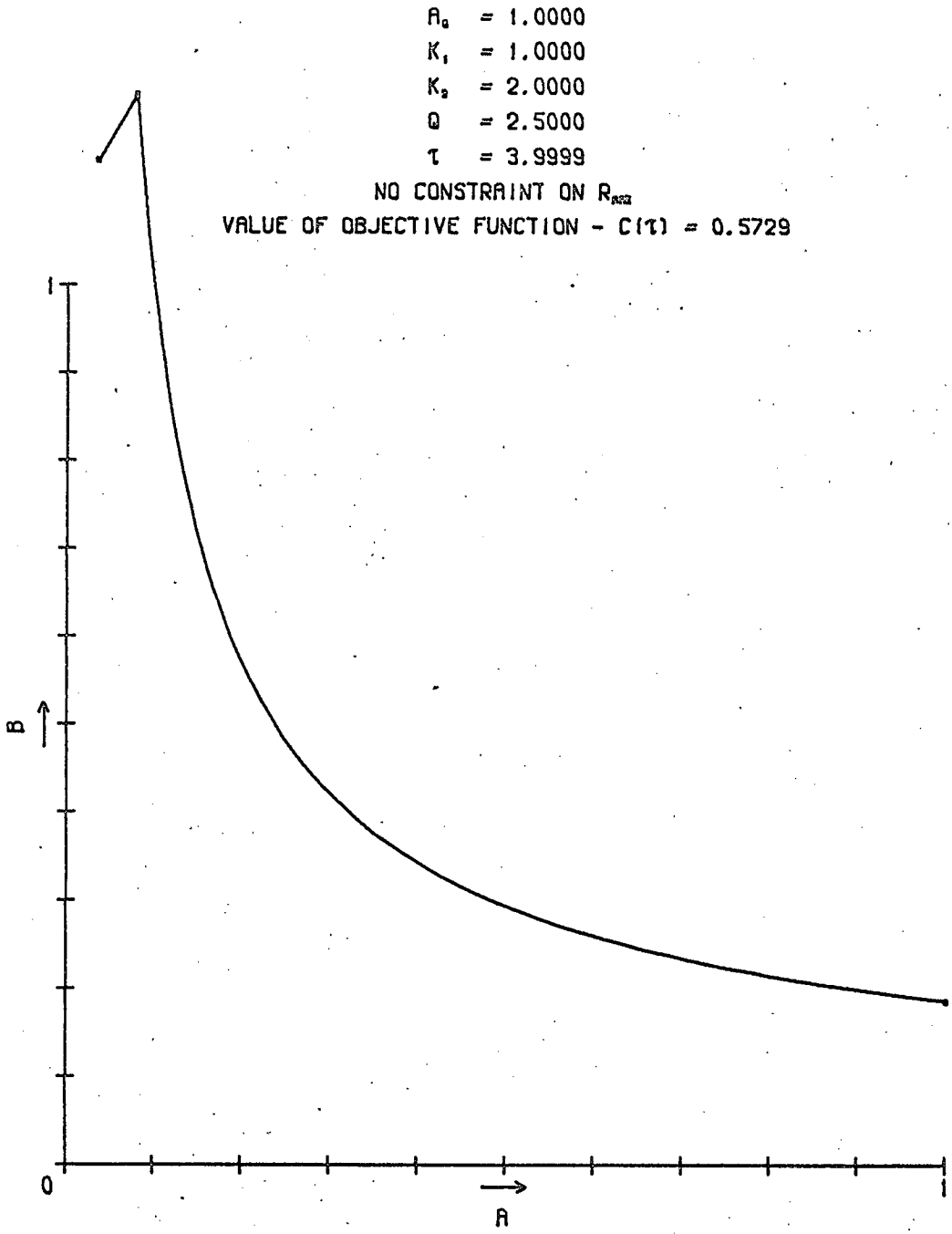
Adjoint variables for the control policy of Graph 4.23

A_0 = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.5000
τ = 3.9999
NO CONSTRAINT ON R_{max}
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5729



Graph 4.26

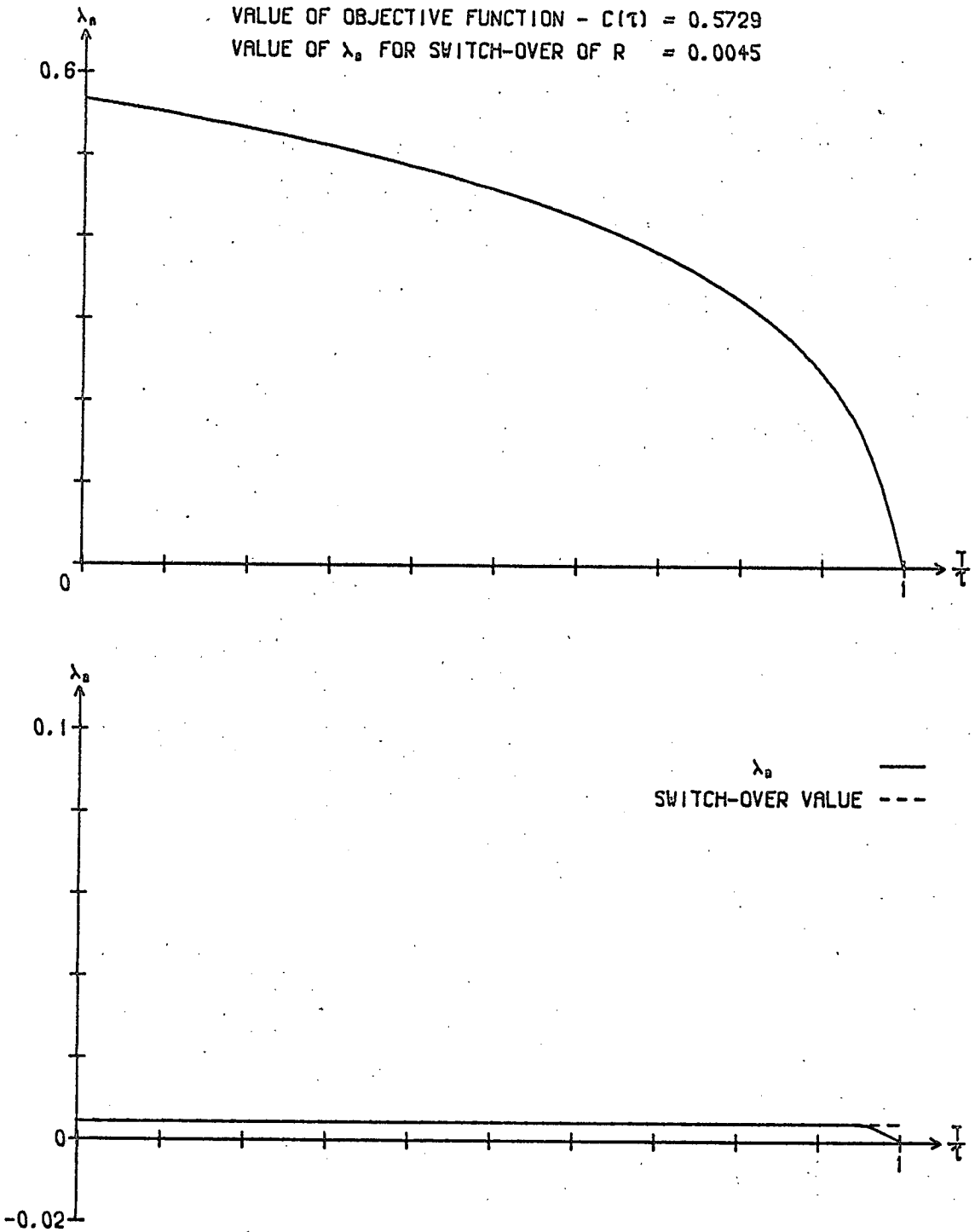
Control policy for Q = 2.5 and r unconstrained.
The initial concentration of B is 0.1857



Graph 4.27

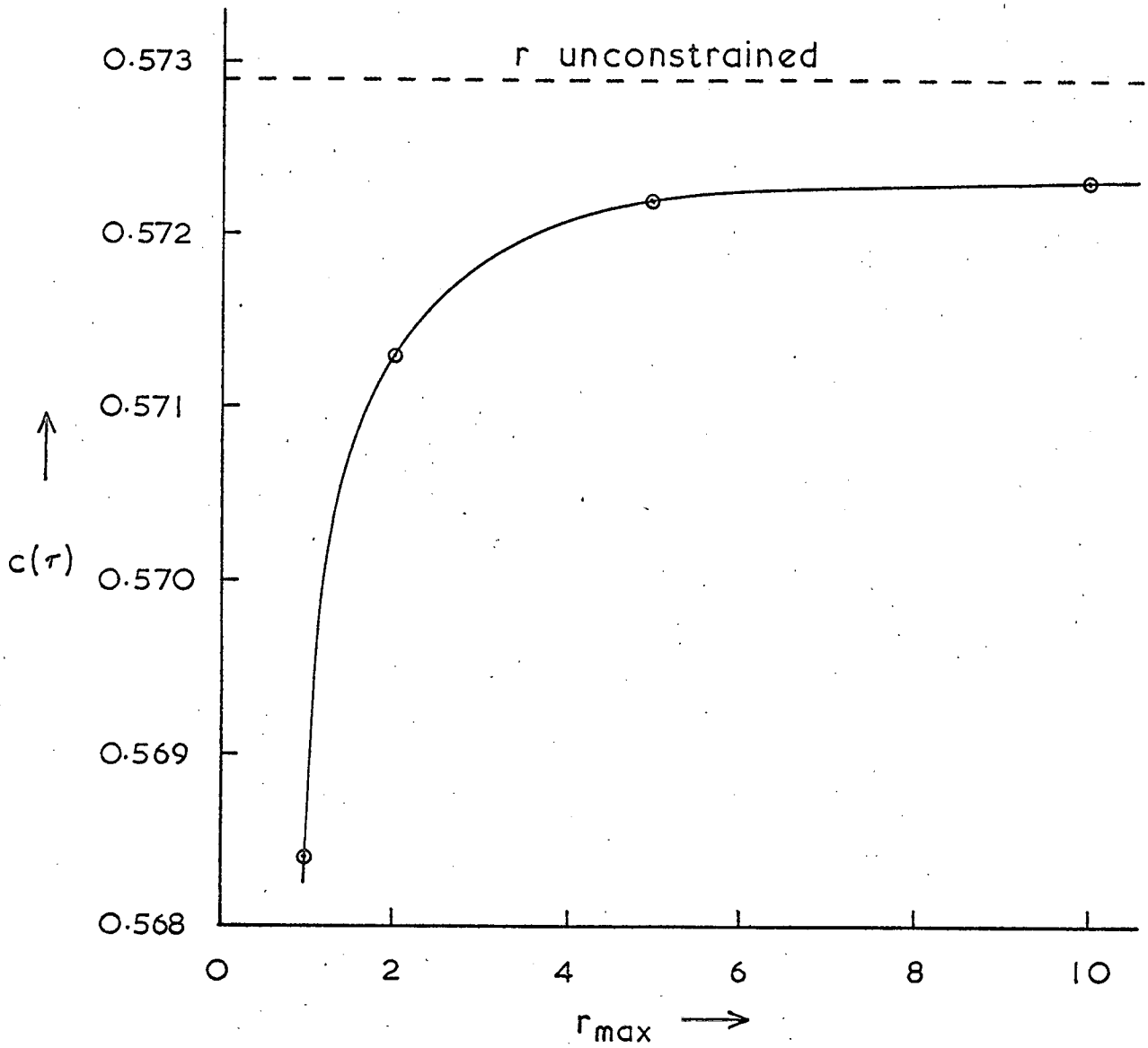
Solution trajectory in the a-b plane for the control policy of Graph 4.26

A_0 = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 2.5000
τ = 3.9999
NO CONSTRAINT ON R_{max}
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5729
VALUE OF λ_0 FOR SWITCH-OVER OF R = 0.0045



Graph 4.28

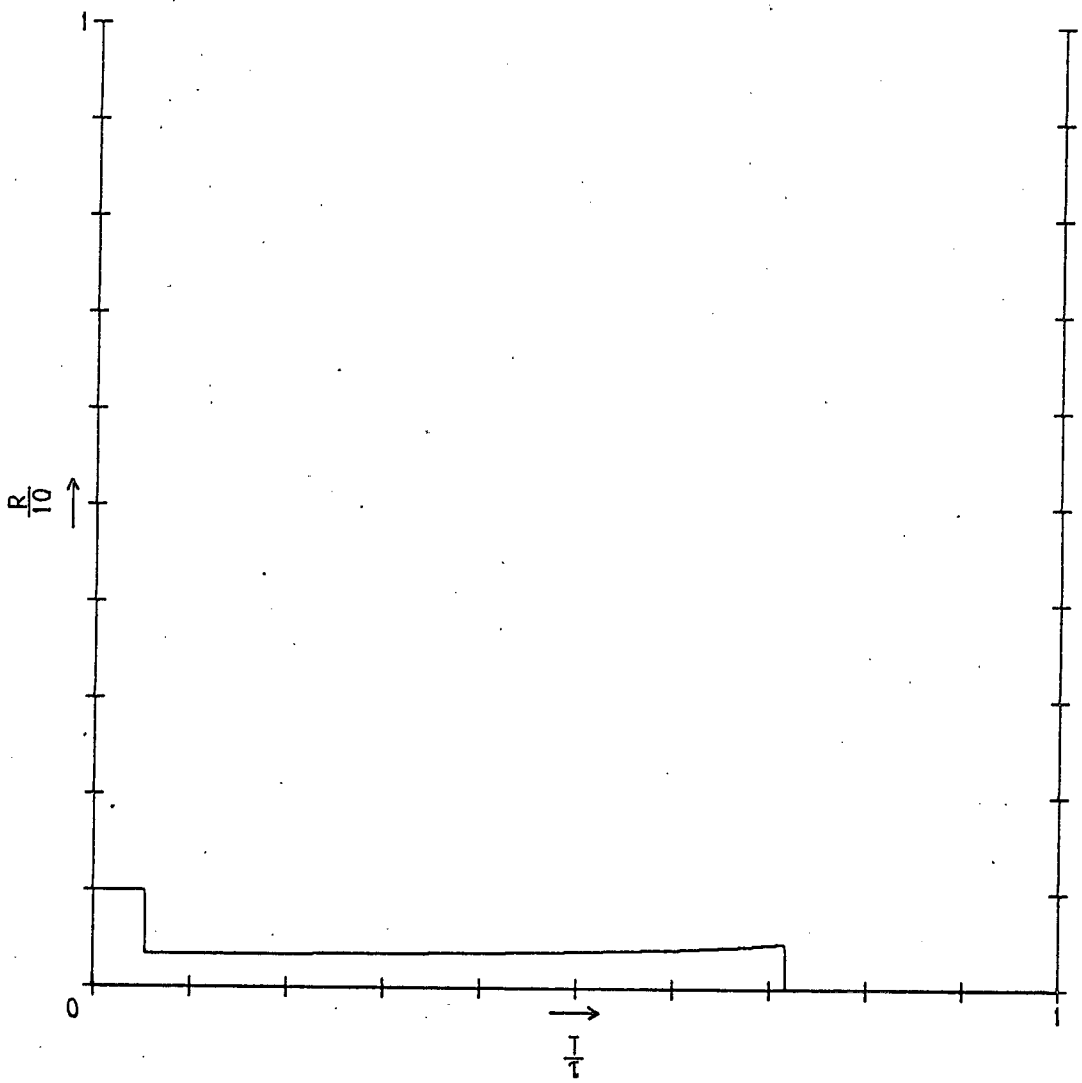
Adjoint variables for the control policy of Graph 4.26



Graph 4.29

Values of $c(\tau)$ for increasing values of r_{max}, and for r unconstrained.
$a_o = 1$, $k_1 = 1$, $k_2 = 2$, batch time $\tau = 4$, and $Q = 2.5$.

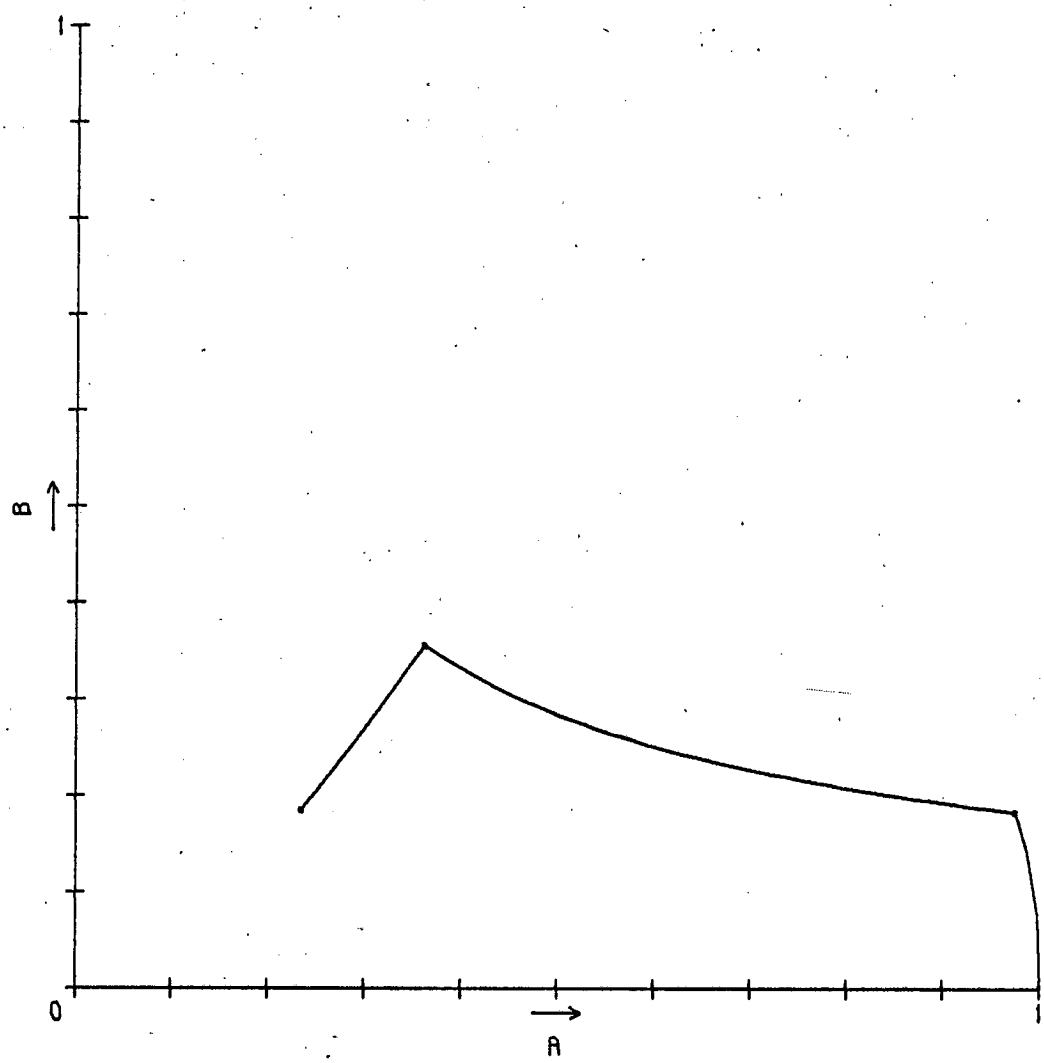
R_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.1999
τ = 3.9996
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5155



Graph 4.30

Control policy for Q = 1.2 and r_{max} = 1

A_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.1999
τ = 3.9996
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5155

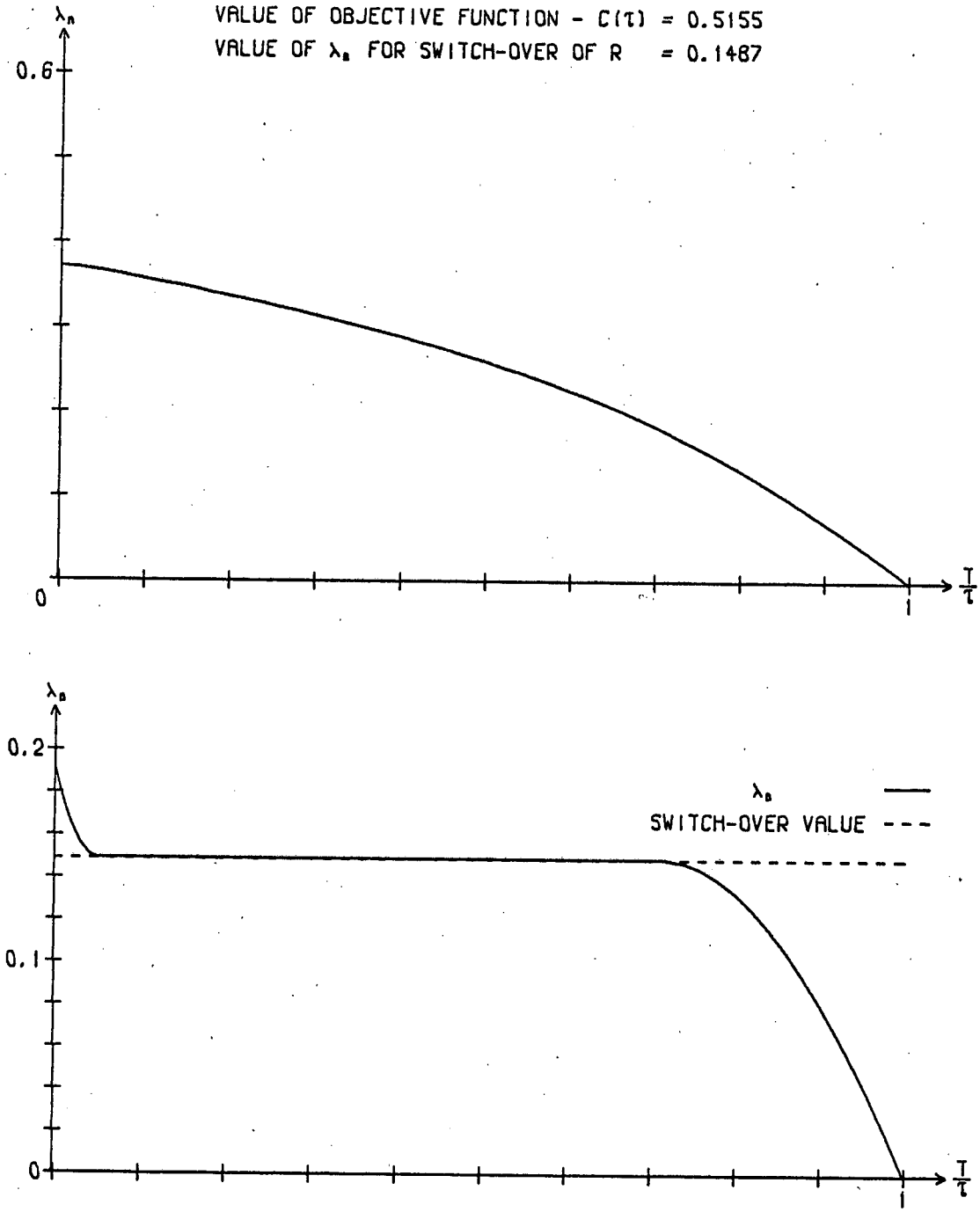


Graph 4.31

Solution trajectory in the a-b plane for the control policy of Graph 4.30

A_0 = 1.0000
R_{max} = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.1999
τ = 3.9996

VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5155
VALUE OF λ_R FOR SWITCH-OVER OF R = 0.1487



Graph 4.32

Adjoint variables for the control policy of Graph 4.30

A_0 = 1.0000

R_{max} = 10.0000

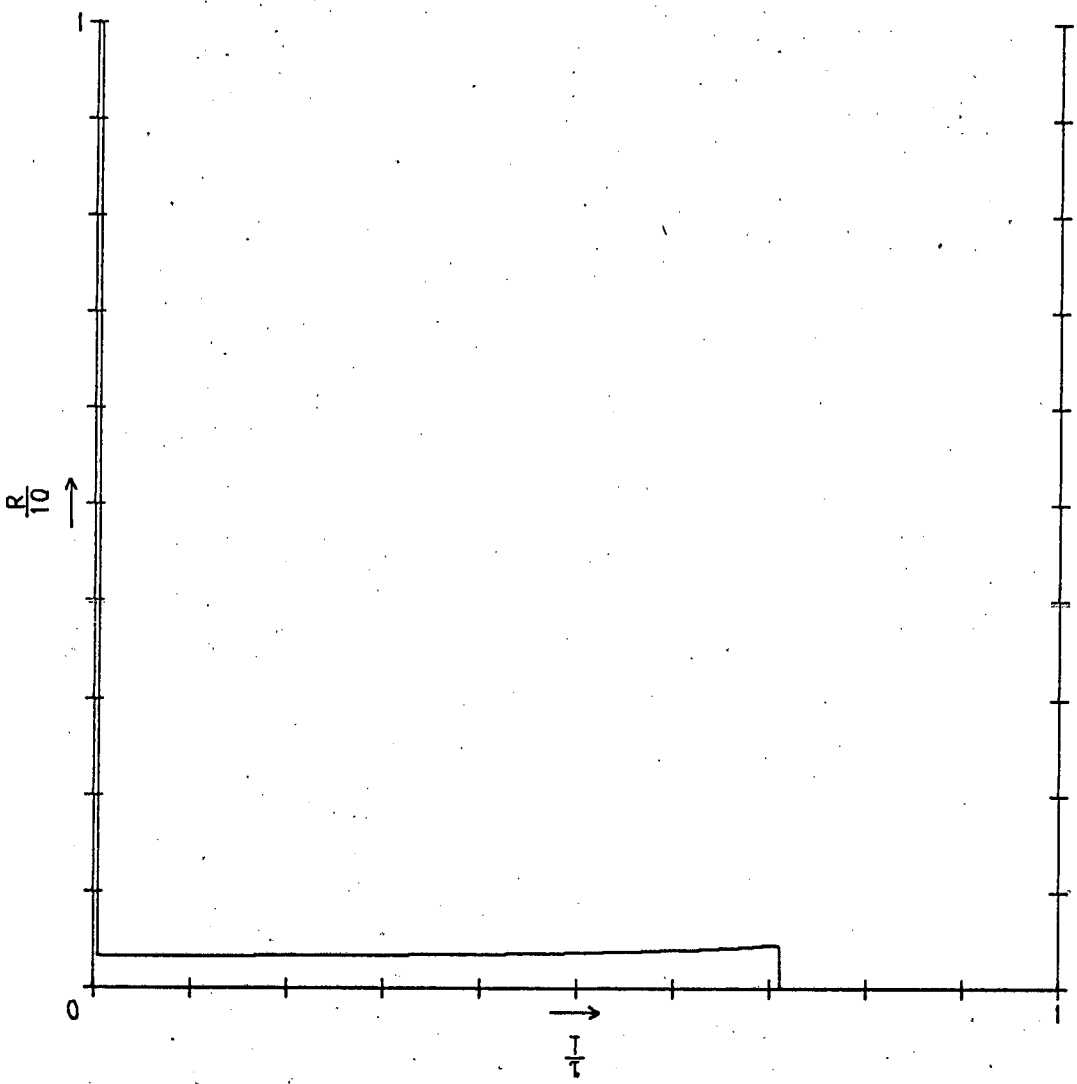
K_1 = 1.0000

K_2 = 2.0000

Q = 1.1999

τ = 3.9994

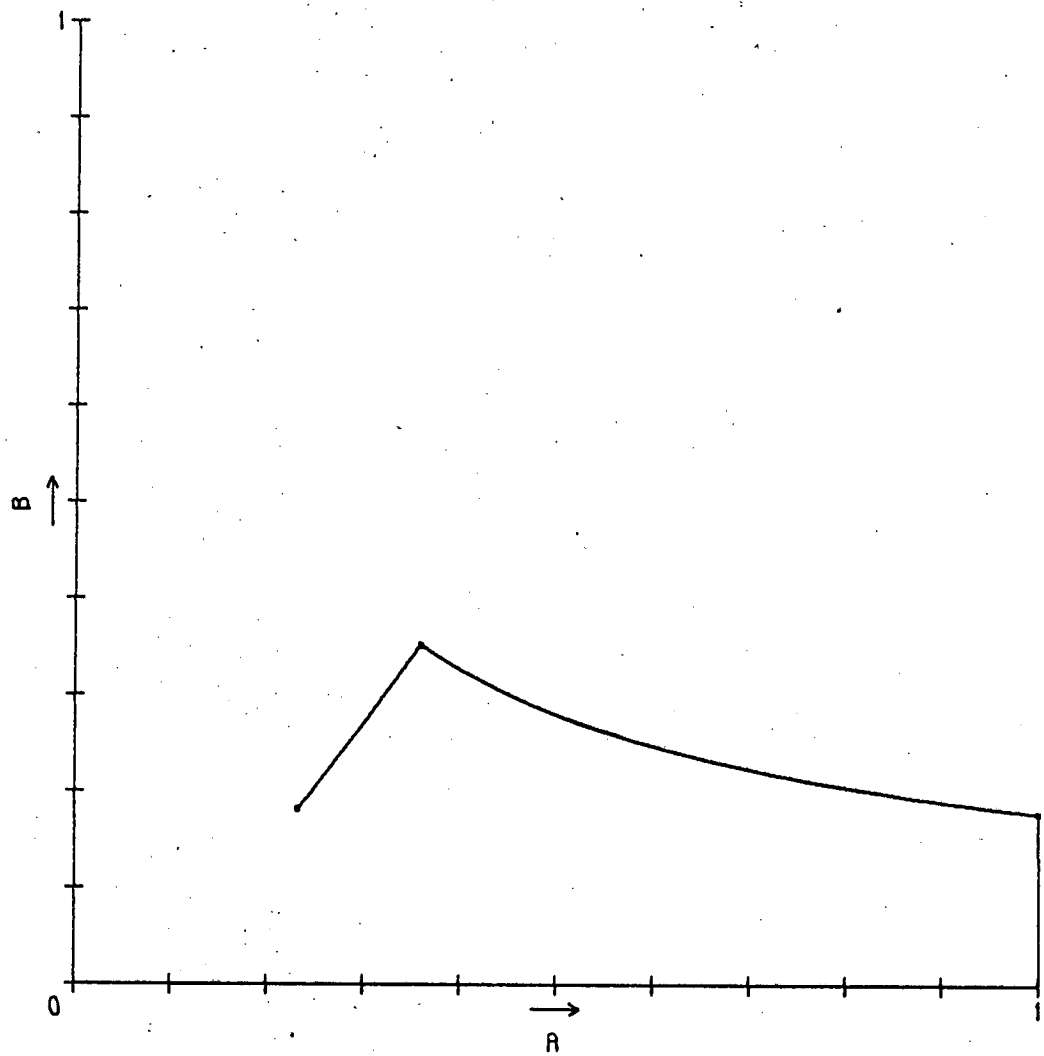
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5180



Graph 4.33

Control policy for Q = 1.2 and r_{max} = 10

A_0 = 1.0000
R_{max} = 10.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.1999
τ = 3.9994
VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.5180

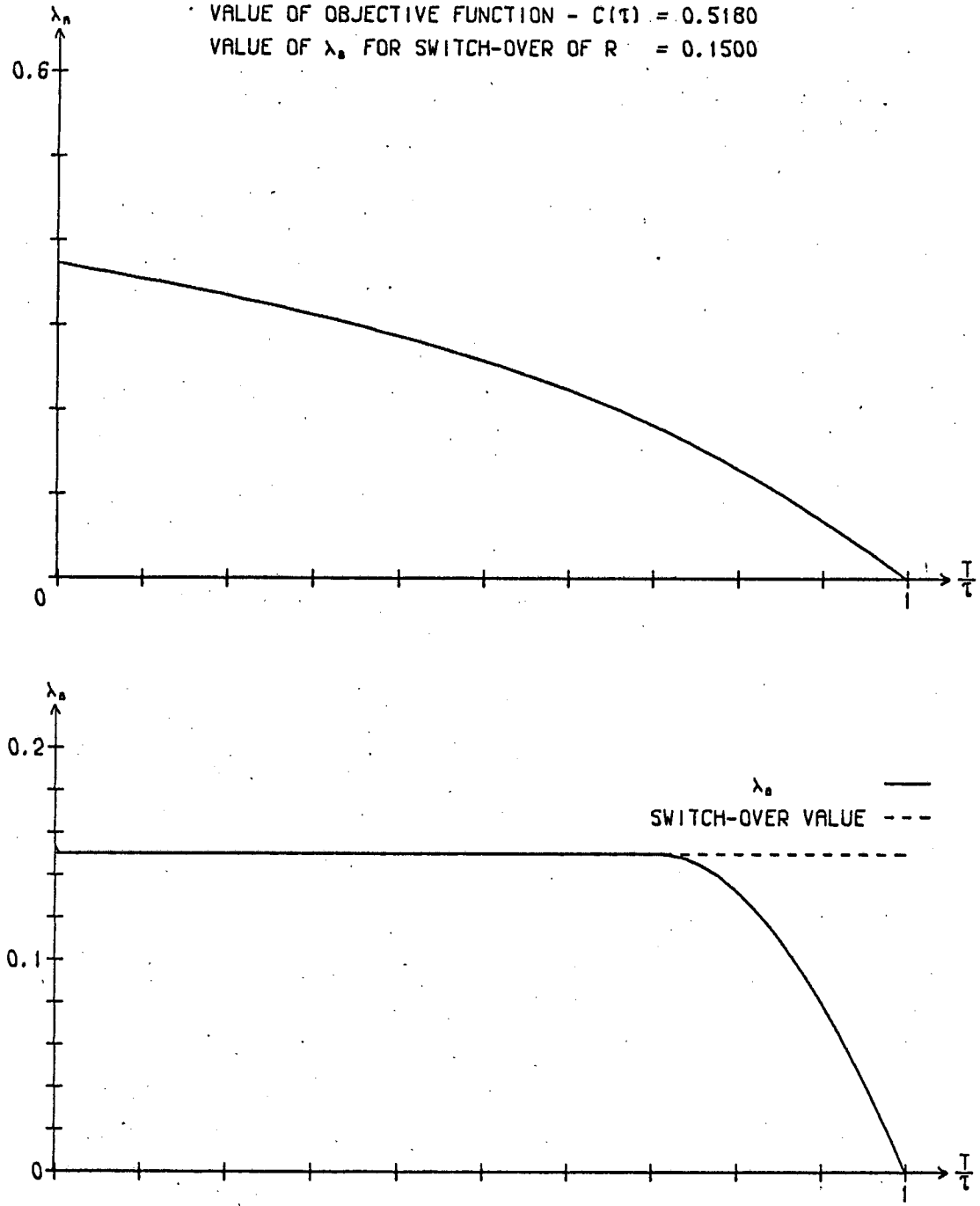


Graph 4.34

Solution trajectory in the a-b plane for the control policy of Graph 4.33

A_0 = 1.0000
R_{max} = 10.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.1999
τ = 3.9994

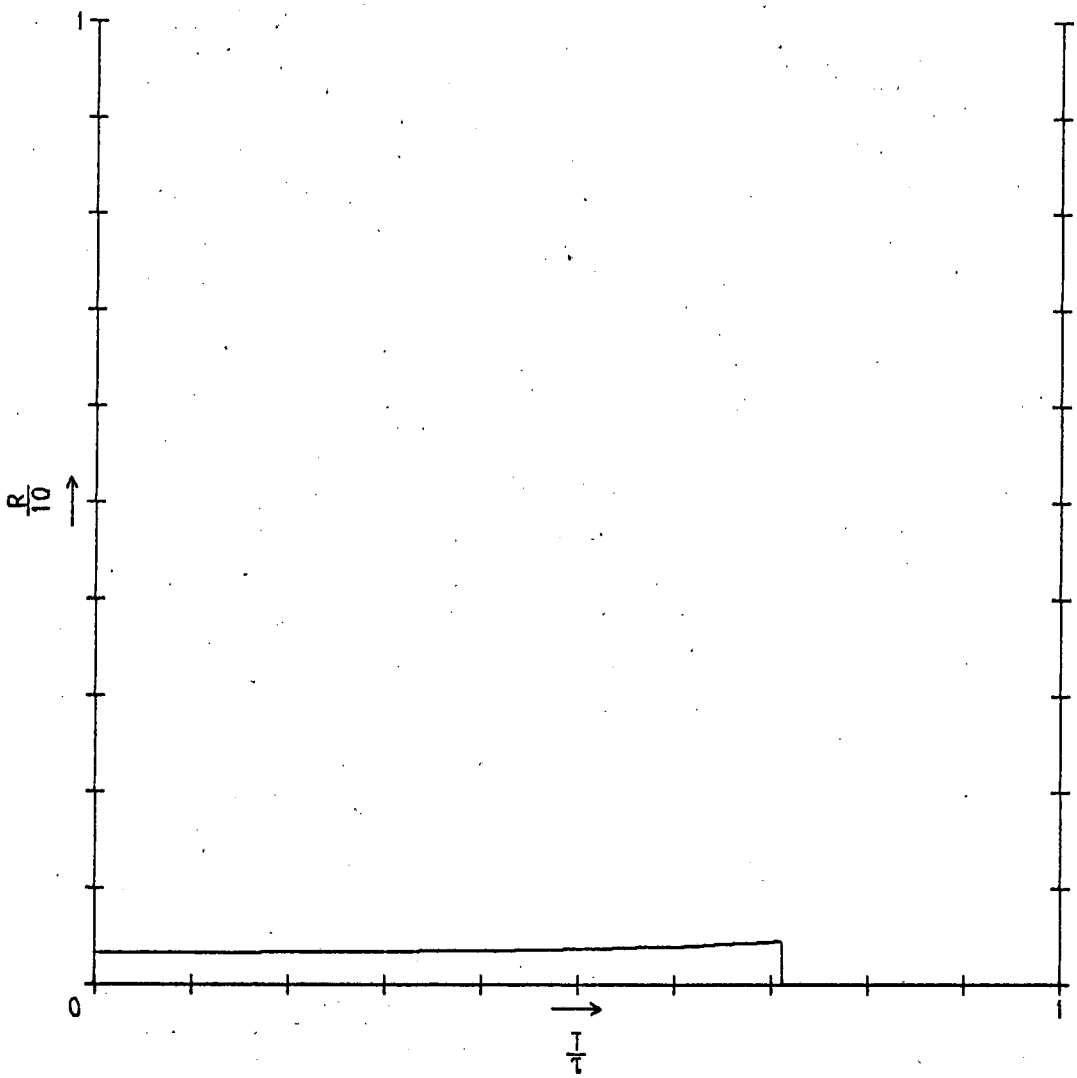
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5180
VALUE OF λ_a FOR SWITCH-OVER OF R = 0.1500



Graph 4.35

Adjoint variables for the control policy of Graph 4.33

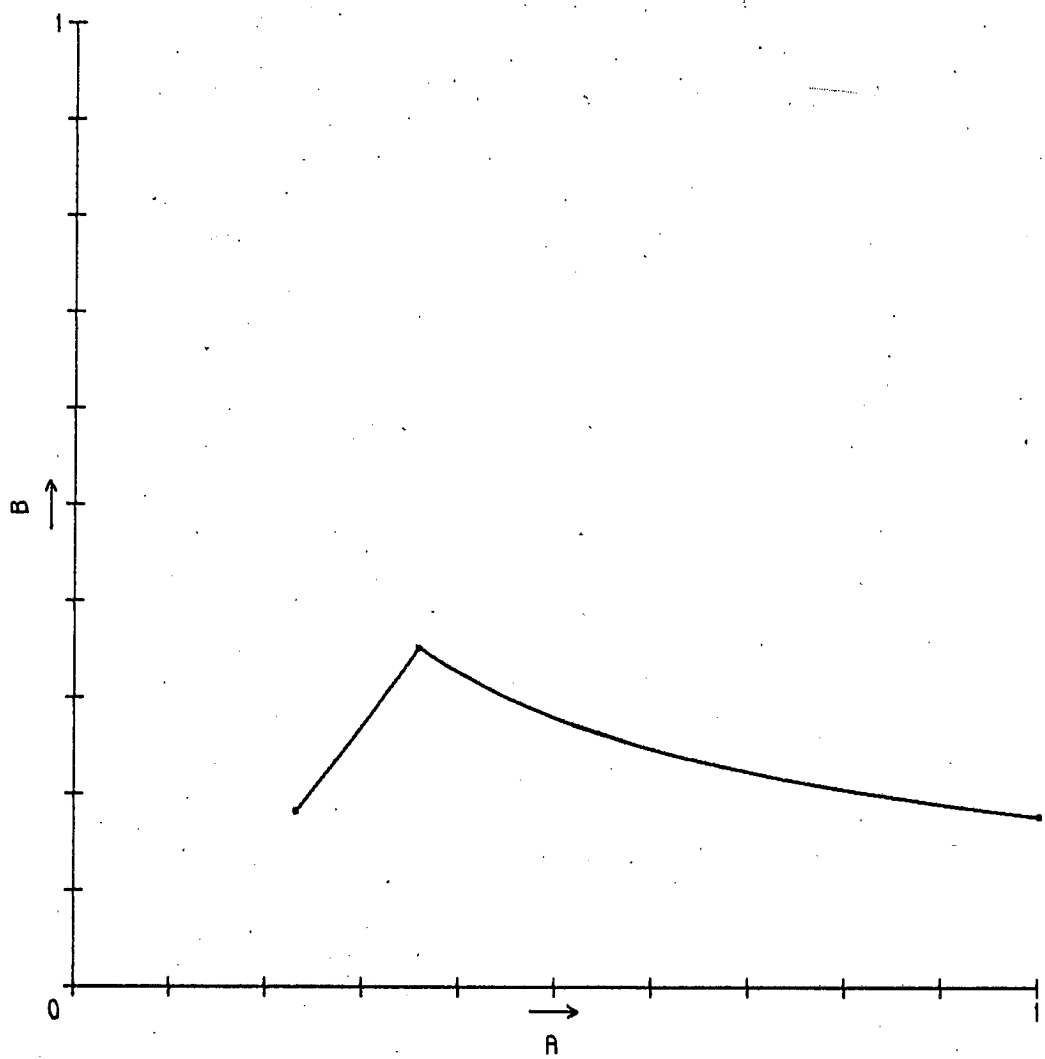
R_0 = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.2000
τ = 3.9996
NO CONSTRAINT ON R_{max}
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5185



Graph 4.36

Control policy for Q = 1.2 and r unconstrained.
The initial concentration of B is 0.1775

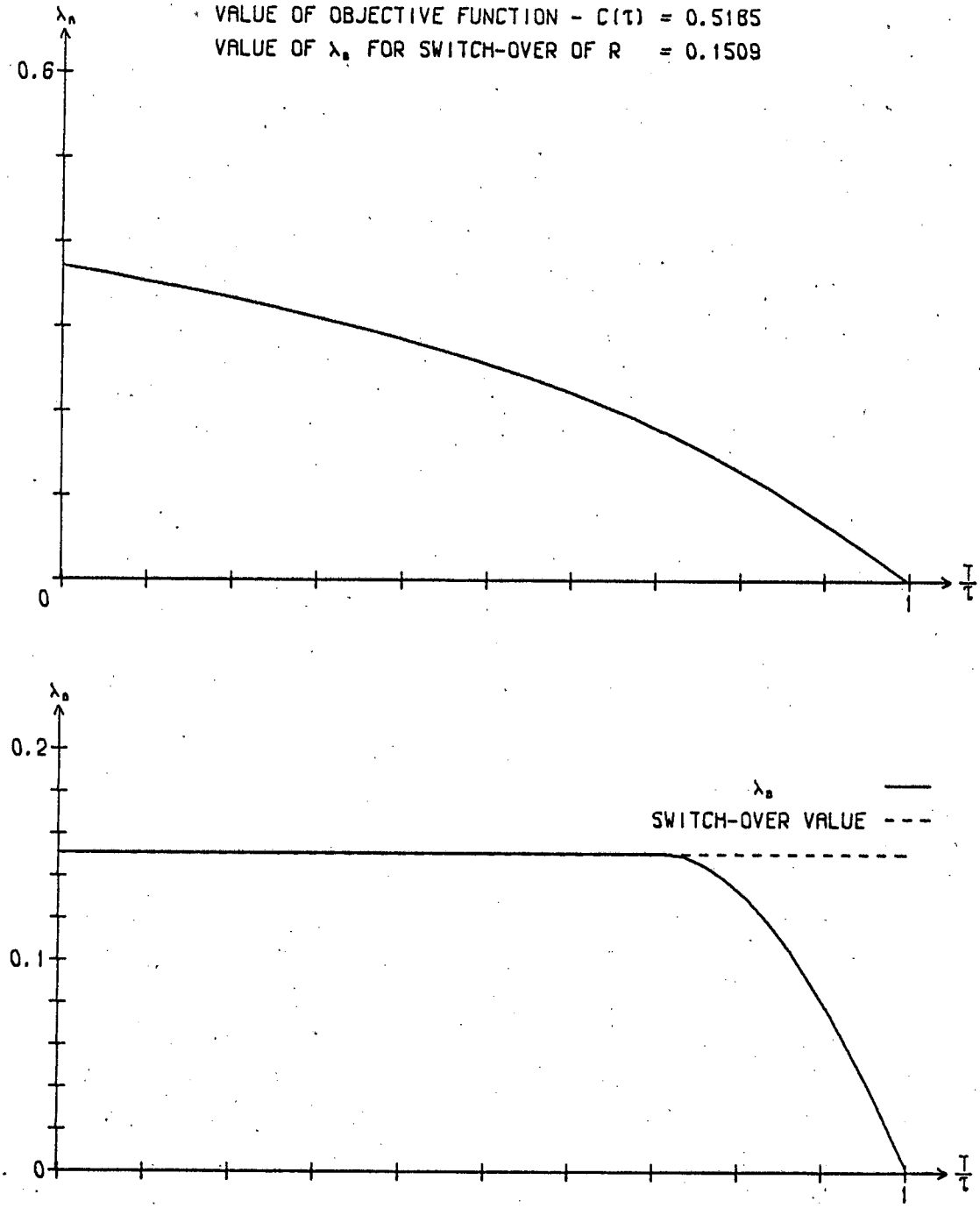
R_0 = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.2000
τ = 3.9996
NO CONSTRAINT ON R_{max}
VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.5185



Graph 4.37

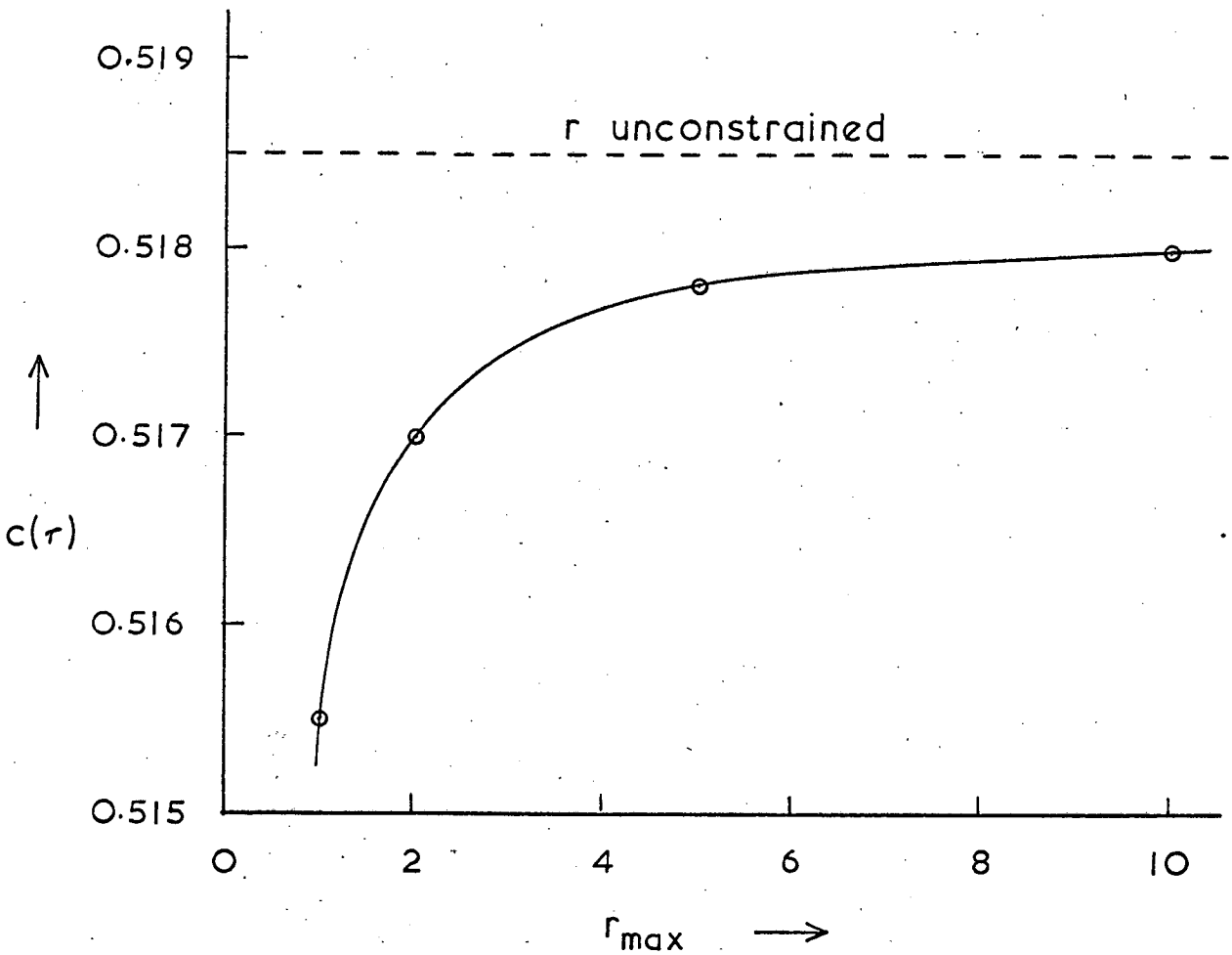
Solution trajectory in the a-b plane for the control policy of Graph 4.36

A_0 = 1.0000
K_1 = 1.0000
K_2 = 2.0000
Q = 1.2000
τ = 3.9996
NO CONSTRAINT ON R_{max}
VALUE OF OBJECTIVE FUNCTION - C(1) = 0.5185
VALUE OF λ_R FOR SWITCH-OVER OF R = 0.1509



Graph 4.38

Adjoint variables for the control policy of Graph 4.36



Graph 4.39

Values of $c(\tau)$ for increasing values of r_{max}, and for r unconstrained. $a_o = 1$, $k_1 = 1$, $k_2 = 2$, batch time $\tau = 4$, and $Q = 1.2$.

Table 4.2

Summary of parameters and results of calculations of trajectories for $Q = 2.5$ (nominally), $\tau = 4$ (nominally), $k_1 = 1$, $k_2 = 2$, $a_o = 1$ and r_{max} varied. Value of $c(\tau)$ for simultaneous addition of the same quantities of A and B at the beginning of the batch is 0.2475.

r_{max}	N	Y	$c(\tau)$	improvement over simultaneous addition
1	0.03540	+ 0.006490	0.5684	129.5%
2	0.04030	- 0.003954	0.5713	130.7%
5	0.03994	- 0.004175	0.5722	131.1%
10	0.03984	- 0.004161	0.5723	131.1%
∞	0.03976	- 0.004445	0.5729	131.4%

Table 4.3

Summary of parameters and results of calculations of trajectories for $Q = 1.2$ (nominally), $\tau = 4$ (nominally), $k_1 = 1$, $k_2 = 2$, $a_o = 1$ and r_{max} varied. The value of $c(\tau)$ for simultaneous addition of the same quantities of A and B at the beginning of the batch is 0.3811

r_{max}	N	Y	$c(\tau)$	improvement over simultaneous addition
1	0.04356	- 0.1487	0.5155	35.3%
2	0.04294	- 0.1495	0.5170	35.7%
5	0.04261	- 0.1499	0.5178	35.9%
10	0.04252	- 0.1500	0.5180	35.9%
∞	0.04240	- 0.1509	0.5185	36.0%

shown in Graphs 4.30 to 4.38. The calculation data and results for this series are summarised in Table 4.3, and the value of the objective function plotted against r_{max} in Graph 4.39.

The singular segments of trajectories for the same value of Q and different values of r_{max} are similar in shape but, as before, are not identical because of differences in the value of γ and N in the calculations (see Appendix I).

It can now be shown that instantaneous addition of a quantity of B at the beginning of the final segment will not satisfy the maximum principle. If such an addition of B is made at this point, the values of λ_a and λ_b remain unaltered from their values on the singular segment, but their derivatives are changed. In particular, in the differential equation for λ_b (equation (3.8))

$$\frac{d\lambda_b}{dt} = k_1 a(\lambda_a + \lambda_b - 1) + 2k_2 ab(\lambda_a + 2\lambda_b)$$

($\lambda_c = 1$ by equation (3.11)), the differential of λ_b is altered by a factor

$$\delta\left(\frac{d\lambda_b}{dt}\right) = 2k_2 a(\lambda_a + 2\lambda_b)\delta q$$

where δq is the quantity of B added. This factor causes an increase in $\frac{d\lambda_b}{dt}$, since all the terms are positive (λ_a on the singular segment is positive in Graphs 4.28 and 4.38, and $\lambda_b = -\gamma > 0$). But $\frac{d\lambda_b}{dt} = 0$ on the singular segment, and so $\frac{d\lambda_b}{dt} > 0$ after this instantaneous addition of B. The greater is δq, the more positive $\frac{d\lambda_b}{dt}$ becomes. Such a situation leads to violation of the maximum principle, as previously mentioned, (p.60)

unless $\delta q = 0$. Therefore there can be no instantaneous addition of a finite quantity of B at the beginning of the final non-singular segment for a trajectory which satisfies the maximum principle.

The values of the objective function for simultaneous addition of A and B at the beginning of the batch are shown for $Q = 2.5$ and $Q = 1.2$ in the captions to Tables 4.2 and 4.3 respectively. For $Q = 2.5$ there is a very striking improvement in the performance of the reactor by distributed addition. The explanation for this is that, with a value of Q of 2.5, which is a large stoichiometric excess for the desired reaction, simultaneous addition of reactants at the beginning of the batch results in high initial concentration of B, which favours the undesired reaction. As a result, reactant A is consumed rapidly initially to form mainly waste product, and so the amount of A left to form desired product later in the reaction is drastically reduced. When the optimal addition-rate policy is followed, the initial concentration of B is kept low (see, for example, Graph 4.15), and there is no high initial rate of consumption of A to form waste products. It is interesting, however, that even such a large stoichiometric excess of B, which gives a poor value of the objective function if added at the beginning of the batch, can be usefully employed if its addition is distributed in the correct manner. It follows from the above arguments that when the value of Q is smaller, and is less of a stoichiometric excess, the improvement of optimal distributed addition over simultaneous addition will be much smaller. This is confirmed in Table 4.3 for the results of $Q = 1.2$.

The results of Tables 4.2 and 4.3 show that, although the objective function is greater for r unconstrained, the increases in the

values over those for $r_{max} = 1$ for the two sets of calculations are both less than 1%. It appears, therefore, that removal of the constraint on r_{max} in this reactor system would be of little practical interest in this case, but with different reactor kinetics or with a different reactor system this may not be true. However, the flattening off of the curve of the value of the objective function against the maximum rate of addition is likely to be general, and so there will exist a value of r_{max} above which there can be little improvement in reactor performance. In a practical environment, evaluation of the objective function for r_{max} unconstrained would then be helpful to establish at what level r_{max} should be set.

CHAPTER 5

SIMULTANEOUS CONTROL OF TEMPERATURE OF REACTION AND RATE OF ADDITION OF REACTANT

It was mentioned in Chapter 1 that regulating the temperature profile of a batch or tubular reactor by some means is probably the most common method of control. It is of interest to find what influence optimal temperature control would have on the performance of a distributed feed tubular reactor or a semi-batch reactor with continuous feed, particularly if the temperature profile and the addition-rate profile are to be simultaneously optimal.

The reactor system investigated in the preceding chapters can again be used for such an investigation. Since this is a preliminary exploration into such a form of control, it will be sensible to keep the reactor system as a simple model, and initially, therefore, the reactor of Chapter 3, where the only constraint is on the maximum rate of addition of B, will be modified for temperature control. For simplicity it will be considered that the temperature of the reactor can be controlled directly, and that there are no temperature gradients of any kind, or other complicating features, in the reactor.

To begin with, this temperature, θ, will be constrained such that

$$\theta_{min} \leq \theta \leq \theta_{max}; \qquad (5.1)$$

later, the effect of letting $\theta_{min} \to 0$ will be considered. For the reactions taking place in the reactor

$$\left.\begin{array}{l} A + B \xrightarrow{k_1} AB \text{ (product)} \\ A + 2B \xrightarrow{k_2} AB_2 \text{ (waste)} \end{array}\right\} \qquad (5.2)$$

the reaction rate constants, k_1 and k_2, are assumed to be of the Arrhenius form

$$k_1 = z_1 \exp\left(\frac{-E_1}{\theta}\right) \qquad (5.3)$$

$$k_2 = z_2 \exp\left(\frac{-E_2}{\theta}\right) \qquad (5.4)$$

where E_1 and E_2 are the activation energies of the reactions (5.2) divided by the value of the Universal Gas Constant.

5.1 The Basic Model

The differential equations for the state variables and for the adjoint variables, together with their boundary conditions, are as for the system of Chapter 3, which simplify by equation (3.11) to

$$\frac{da}{dt} = -k_1 ab - k_2 ab^2 \quad ; \quad a(0) = a_o \qquad (5.5)$$

$$\frac{db}{dt} = -k_1 ab - 2k_2 ab^2 + r \quad ; \quad b(0) = 0 \qquad (5.6)$$

$$\frac{dc}{dt} = k_1 ab \quad ; \quad c(0) = 0 \qquad (5.7)$$

$$\frac{d\lambda_a}{dt} = k_1 b(\lambda_a + \lambda_b - 1) + k_2 b^2(\lambda_a + 2\lambda_b) \quad ; \quad \lambda_a(\tau) = 0 \qquad (5.8)$$

$$\frac{d\lambda_b}{dt} = k_1 a(\lambda_a + \lambda_b - 1) + 2k_2 ab(\lambda_a + 2\lambda_b) \quad ; \quad \lambda_b(\tau) = 0 \qquad (5.9)$$

$$\frac{d\lambda_c}{dt} = 0 \quad ; \quad \lambda_c(\tau) = 1 \qquad (5.10)$$

where the objective function is again

$$P = c(\tau) , \tag{5.11}$$

The Hamiltonian is as before

$$H = r\lambda_b - k_1 ab(\lambda_a + \lambda_b - 1) - k_2 ab^2(\lambda_a + 2\lambda_b). \tag{5.12}$$

For optimal temperature and rate of addition controls, this must be maximised with respect to both θ and r, with the adjoint and state variables considered constant for this maximisation.

5.1.1 Control of r

As the Hamiltonian is linear in r a singular segment can occur, as previously, for which the values of λ_a and λ_b are given by

$$\lambda_a = \frac{k_1}{k_1 + 2k_2 b} \quad ; \quad \lambda_b = 0 . \tag{5.13}$$

Considerable information about the value of θ to maximise H can be obtained from the partial derivative of H with respect to θ

$$\frac{\partial H}{\partial \theta} = - \frac{k_1 E_1}{\theta^2} ab(\lambda_a + \lambda_b - 1) - \frac{k_2 E_2}{\theta^2} (\lambda_a + 2\lambda_b) . \tag{5.14}$$

Substituting the values of λ_a and λ_b given by equation (5.13) leads to

$$\left(\frac{\partial H}{\partial \theta}\right)_{\text{singular segment}} = \frac{k_1 k_2 ab^2 (2E_1 - E_2)}{(k_1 + 2k_2 b)\theta^2} . \tag{5.15}$$

The temperature of the reactor can take values between its limits only when such a temperature can cause $\frac{\partial H}{\partial \theta}$ to be zero. On a

singular segment, the value of $\frac{\partial H}{\partial \theta}$ given by equation (5.15) is non-zero for all values of θ unless $E_2 = 2E_1$, and therefore for all but these relative activation energies the temperature of the reactor during the singular segment must be at one of its limits. As the only time when r can take values between its limits is on a singular segment, it follows that the rate of addition of B and the temperature of the reactor cannot simultaneously take values between their limits.

From equation (5.15) it is seen that the Hamiltonian is maximised with respect to θ on the singular segment when

$$\left.\begin{aligned} \theta &= \theta_{max} \text{ for } E_2 < 2E_1 \\ \theta &= \theta_{min} \text{ for } E_2 > 2E_1. \end{aligned}\right\} \qquad (5.16)$$

For $E_2 \neq 2E_1$ the singular segment is therefore isothermal, and the rate of addition on the singular segment can be obtained as before by differentiating λ_a as given in equation (5.13) with respect to time

$$\frac{d\lambda_a}{dt} = \frac{\frac{2k_1k_2b}{\theta^2}(E_1 - E_2)\frac{d\theta}{dt} + 2k_2\frac{db}{dt}}{(k_1 + 2k_2b)^2} . \qquad (5.17)$$

Substituting for $\frac{db}{dt}$ by equation (5.6), and comparing the result with equation (5.8) in which equations (5.13) have been substituted for λ_a and λ_b, leads to an equation for r on the singular segment:

$$r = b(k_1 + 2k_2b)(a + \frac{b}{2}) - \frac{b}{\theta^2}(E_2 - E_1)\frac{d\theta}{dt} . \qquad (5.18)$$

But it has already been shown that, during the singular segment, θ is constant unless $E_2 = 2E_1$ (equation (5.16)). Thus, on the singular

segment, provided $E_2 \neq 2E_1$, r is given by the familiar equation

$$r = b(k_1 + 2k_2 b)(a + \frac{b}{2}). \tag{5.19}$$

The equation for the singular segment is obtained as before by comparison of the value of the Hamiltonian on the singular segment with its value at $t = \tau$. In this case, the Hamiltonian at $t = \tau$ is given by

$$H_\tau = k_1 a(\tau) b(\tau) \tag{5.20}$$

which is maximised by $\theta = \theta_{max}$, since k_1 takes its maximum value at this temperature. Thus

$$\begin{aligned} H_{max} &= k_1(\theta = \theta_{max})\ a(\tau)b(\tau) \\ &= k_1(\theta = \theta_{max})N \end{aligned} \tag{5.21}$$

and the equation for the singular segment becomes

$$k_1(\theta = \theta_{max})N = \frac{k_1 k_2 a b^2}{k_1 + 2k_2 b} \tag{5.22}$$

where the right hand side of the equation is evaluated at $\theta = \theta_{max}$ or $\theta = \theta_{min}$ depending on the relative values of E_1 and E_2, as governed by equation (5.16).

The form of the singular segment in the a - b plane is again as shown in curve B of Graph 3.4, and as before there is only one singular segment for each pair of $a(\tau)$, $b(\tau)$ lying on the terminal hyperbola

$$a(\tau)b(\tau) = N \quad \text{(equation (3.42))}.$$

The curves C, D and E in Graph 3.4 are for $r = r_{max}$ at constant temperature. Although in this problem it is likely that the temperature

may vary along such non-singular segments, it can be seen intuitively that such variations of temperature can affect the slopes of these curves to only a limited extent. It can be shown in the same way as in Chapter 3 that $r = r_{max}$ at $t = 0$ and at $t = \tau$, and therefore the optimal sequence of control of r is probably of the same form as that found in Chapter 3, viz.

(a) initial non-singular segment, with $r = r_{max}$ at $t = 0$

(b) singular segment, with r governed by equation (5.19)

(c) final non-singular segment, with $r = r_{max}$ at $t = \tau$.

It is again likely that no bang-bang switching of r will occur during the non-singular segments, but this can be ascertained only by calculation.

5.1.2 Control of θ

It has already been shown that $\theta = \theta_{max}$ at $t = \tau$ and that, for $E_2 \neq 2E_1$, θ is constant during the singular segment, governed by equation (5.16). It appears that θ can take values between its limits for $E_2 \neq 2E_1$ only on a non-singular segment. For such intermediate values of θ, if they occur, it must also be true that $\frac{\partial H}{\partial \theta} = 0$ and that the Hamiltonian shows a maximum at this value of θ.

Horn {48} has pointed out that when only two independent reactions are involved, as here, the adjoint variables λ_a and λ_b can be eliminated between the equations (5.5), (5.6), (5.8), (5.9), and equation (5.14) set to zero, to give an explicit expression for $\frac{d\theta}{dt}$ in terms of a, b and θ. However, since this result derives from the weak condition

of a stationary Hamiltonian it should be used with caution. Thus, setting equation (5.14) for $\frac{\partial H}{\partial \theta}$ to zero, the condition

$$\lambda_a = \frac{k_1E_1 - (k_1E_1 + 2k_2E_2b)\lambda_b}{k_1E_1 + k_2E_2b} \tag{5.23}$$

is obtained. Differentiating this with respect to time, and making similar substitutions to those in deriving equation (5.18) leads to

$$\frac{d\theta}{dt} = \frac{(2a + b)(k_1E_1 + k_2E_2b)}{E_1E_2}\,\theta^2 - \frac{r(t)\theta^2}{b(E_2 - E_1)} \tag{5.24}$$

where r(t) is the rate of addition of component B.

When $E_2 > 2E_1$, $\theta = \theta_{min}$ at the end of the singular segment and $\theta = \theta_{max}$ at $t = \tau$. For this situation the temperature must transfer during the final non-singular segment from θ_{min} to θ_{max} by either a section of intermediate θ, with θ varying according to equation (5.24), or by a discontinuous switch of θ from one limit to the other. However, it is readily shown, as follows, that for $E_2 > 2E_1$ such switching of θ cannot satisfy the maximum principle.

If instantaneous switching of θ from one limit to the other is to satisfy the maximum principle, then $\frac{\partial H}{\partial \theta}$ must be positive for $\theta = \theta_{max}$ and negative for $\theta = \theta_{min}$. In other words, the Hamiltonian must show a minimum at some value of θ between θ_{min} and θ_{max}. From equation (5.14), the following inequality must hold at $\theta = \theta_{max}$

$$\frac{k_1E_1}{\theta^2}\,ab(1 - \lambda_a - \lambda_b) > \frac{k_2E_2}{\theta^2}\,ab^2(\lambda_a + 2\lambda_b)$$

which simplifies to

$$\left(\frac{k_1}{k_2}\right)_{\theta = \theta_{max}} E_1(1 - \lambda_a - \lambda_b) > E_2b(\lambda_a + 2\lambda_b). \tag{5.25}$$

At $\theta = \theta_{min}$, this inequality must be reversed if instantaneous switching of θ is to satisfy the maximum principle. For reversal of this inequality, we must certainly have

$$\left(\frac{k_1}{k_2}\right)_{\theta = \theta_{min}} < \left(\frac{k_1}{k_2}\right)_{\theta = \theta_{max}} . \tag{5.26}$$

Substituting for k_1 and k_2 by equations (5.3) and (5.4) respectively, this simplifies to

$$E_2 < E_1 . \tag{5.27}$$

It follows, therefore, that instantaneous switching of θ between its limits cannot satisfy the maximum principle if $E_2 > E_1$.

Thus, for $E_2 > 2E_1$ an instantaneous switch of temperature from θ_{min} to θ_{max} during the final non-singular segment cannot form part of the solution trajectory, and a section (or sections) of the final segment in which θ changes smoothly must occur.

For $E_2 < 2E_1$, $\theta = \theta_{max}$ both during the singular segment and at $t = \tau$. A section of θ between its limits is not necessary for the final non-singular segment as it is for $E_2 > 2E_1$, but whether or not such values of θ occur can be determined only by calculation of $\frac{\partial H}{\partial \theta}$ along this segment.

Because of the increased complexity of the temperature control problem over the simple isothermal rate of addition situation, it is difficult to make any further conclusive deductions about the form of control. It is in this sort of situation that the method of Gradients in Function Space can give some useful indications. Since very little is

known about the required temperature profile, any initial policy for such a search will almost certainly be a very poor approximation to the final result. Therefore the simplest form of the Gradients in Function Space algorithm described in Chapter 3 must be used.

5.1.3 Gradients in Function Space Solution

The "gradient" functions for this method of solution are given by the partial derivatives of the Hamiltonian with respect to the control variables:

$$\delta r = \frac{\partial H}{\partial r} = \lambda_b \qquad (5.28)$$

$$\delta\theta = \frac{\partial H}{\partial \theta} = -\frac{k_1 E_1}{\theta^2} ab(\lambda_a + \lambda_b - 1) - \frac{k_2 E_2}{\theta^2} ab^2(\lambda_a + 2\lambda_b). \qquad (5.29)$$

In contrast to the situation in Chapter 3, where it was found more efficient to find a suitable value of the parameter ε and to re-evaluate the gradient function after each step, there are distinct improvements in terms of convergence on this occasion in finding first the value of ε_1 for δr to approximately maximise the objective function for the old gradient function, and then to similarly maximise the objective function with respect to ε_2 for $\delta\theta$. Only after these maximisations are new gradient functions evaluated.

For the first searches the initial profiles used were $r = r_{max}$ throughout and $\theta = 300^{\circ}C$ throughout. All the searches were made with the following items of data in common:

$E_1 = 5000 \quad (z_1 = 6161)$

$a_o = 1$

$r_{max} = 1$

$\theta_{min} = 250^oC, \quad \theta_{max} = 350^oC$

$\tau = 4$

z_1 and z_2 chosen so that $k_1 = 1$, $k_2 = 2$ at 300^oC.

These correspond at 300^oC to the standard system parameters used for many of the previous calculations, and so the results of Graphs 3.8 to 3.10 can be used for comparison purposes.

The final trajectories for $E_2 = 0.9E_1$ and for $E_2 = 1.5E_1$ are shown in Graphs 5.1 to 5.3 and 5.5 to 5.7 respectively. It is seen that the temperature control consists quite distinctly of $\theta = \theta_{max}$ throughout, and the rate of addition profile is similar to that obtained when there was no temperature control. When $E_2 > 2E_1$, however, the temperature cannot be at its maximum value throughout, and this is shown in Graphs 5.9 to 5.11 for $E_2 = 2E_1$, and in Graphs 5.13 to 5.15 for $E_2 = 3E_1$. It appears that, within the "rounding off" approximations inherent in this method of solution, $\theta = \theta_{max}$ initially and finally, and $\theta = \theta_{min}$ during the singular segment. Between these isothermal sections, θ changes rapidly from one limit to the other. The oscillations in the temperature profile in Graph 5.9 are almost certainly not significant. They appear to be a form of numerical instability, probably resulting from the discretisation of the continuous profiles (the time interval $0 \rightarrow \tau$ was divided into 100 steps for calculations), and appear to occur at points of rapid change of a control variable. Such oscillations have also been observed by Thomas and Wood {49} in the solution of an optimal catalyst blend

R_0 = 1.0000

R_{max} = 1.0000

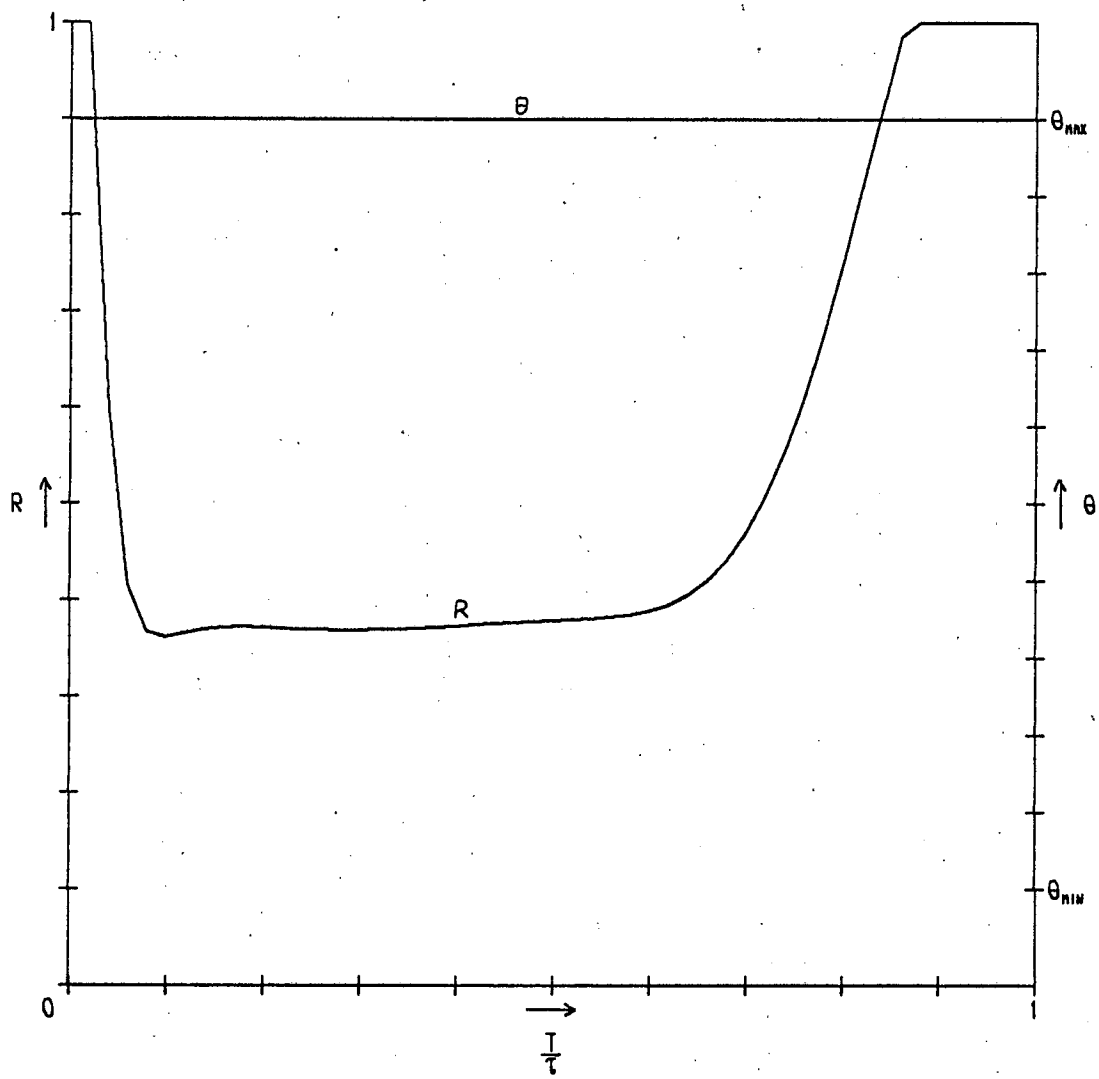
τ = 4.0000

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 5.1490 x 10^3 EXP(-4500/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.689



Graph 5.1

Control policies obtained by the method of Gradients in Function Space for E_2/E_1 = 0.9 .

A_0 = 1.0000

R_{max} = 1.0000

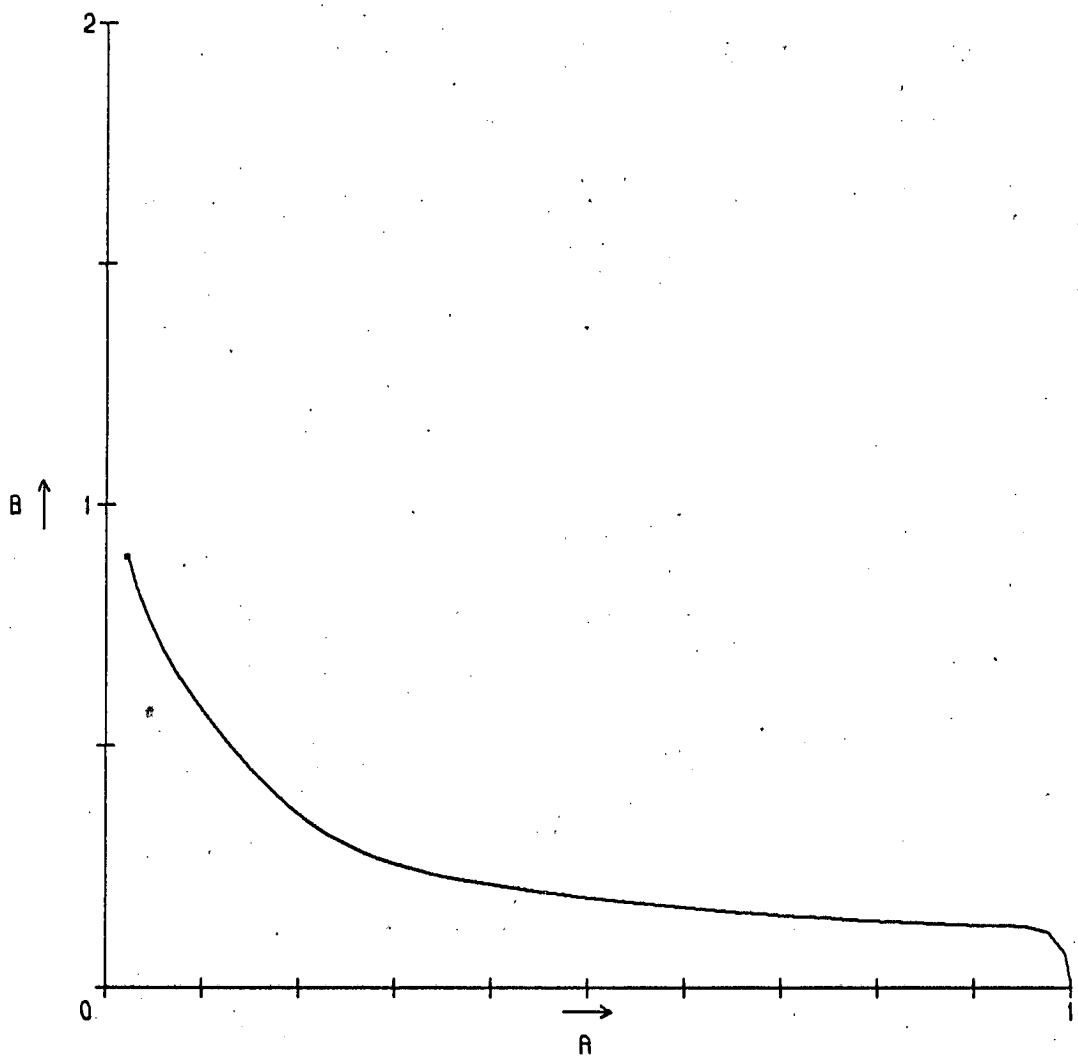
τ = 4.0000

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 5.1490 x 10^3 EXP(-4500/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.689



Graph 5.2

Solution trajectory in the a-b plane for the control policies of Graph 5.1 .

R_0 = 1.0000

R_{max} = 1.0000

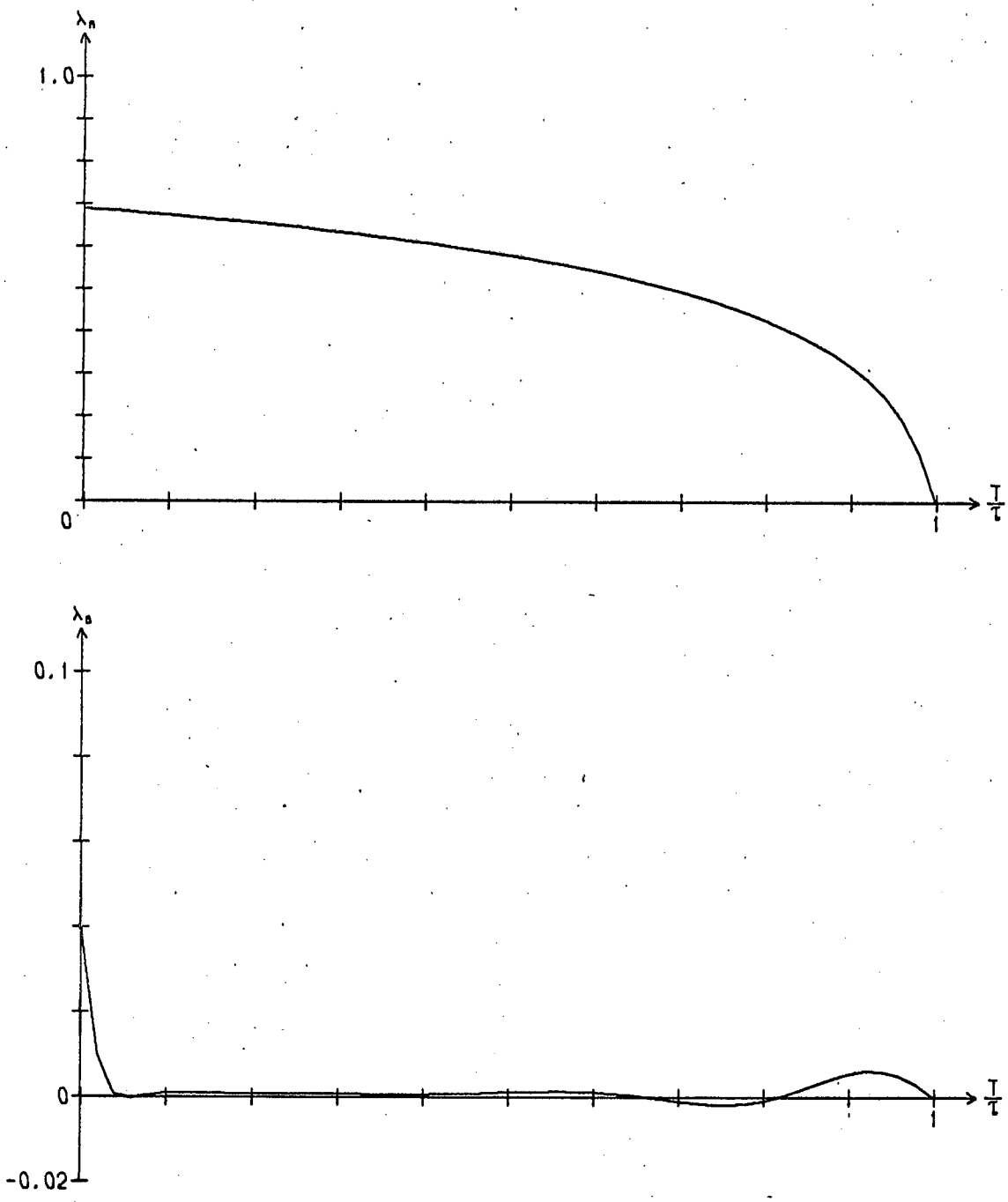
τ = 4.0000

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 5.1490 x 10^3 EXP(-4500/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.689

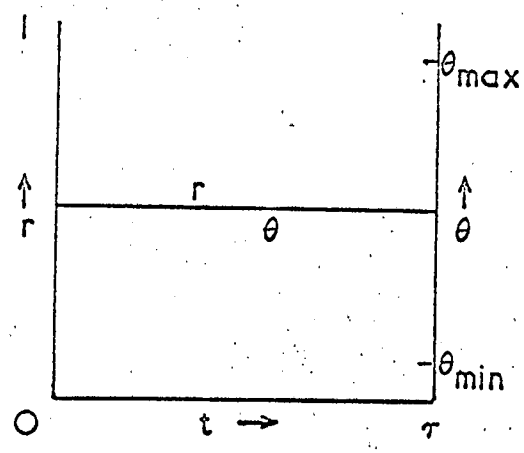


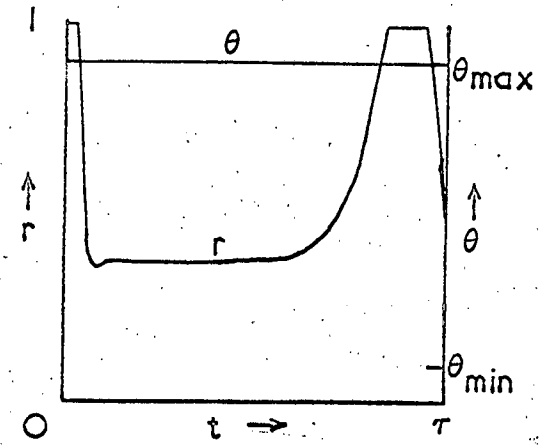
Graph 5.3

Adjoint variables for the control policies of Graph 5.1 .

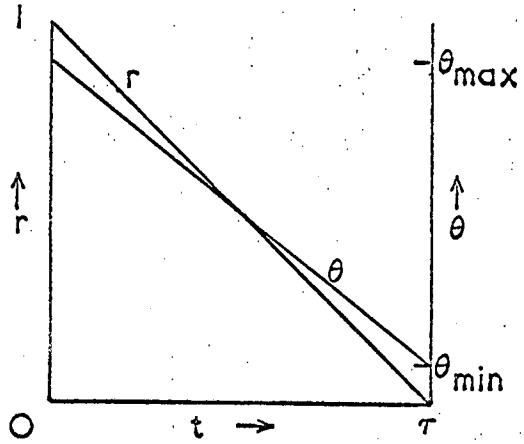
initial profiles

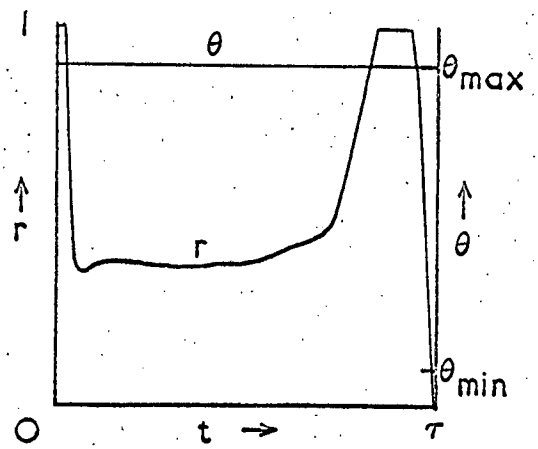
final profiles



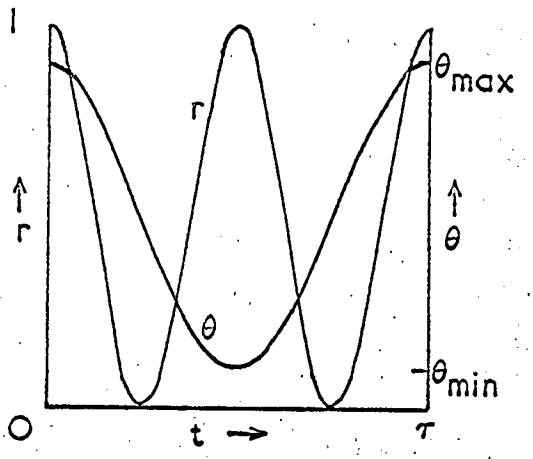


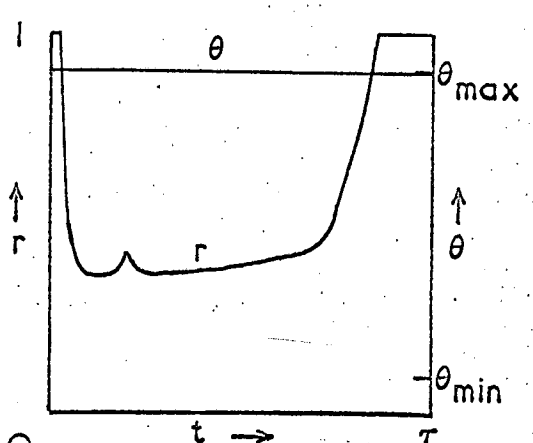
(a) Value of objective function = 0.689.





(b) Value of objective function = 0.689.





(c) Value of objective function = 0.689.

Graph 5.4

Graphs of different initial and resultant final control profiles for Gradient in Function Space searches for the optimal addition-rate and temperature policies. $a_o = 1$, $k_1 = 1$ and $k_2 = 2$ at 300°C, $\theta_{min} = 250°C$, $\theta_{max} = 350°C$, $r_{max} = 1$, $E_1 = 5000$, $E_2 = 4500$ and batch time $\tau = 4$.

A_0 = 1.0000

R_{max} = 1.0000

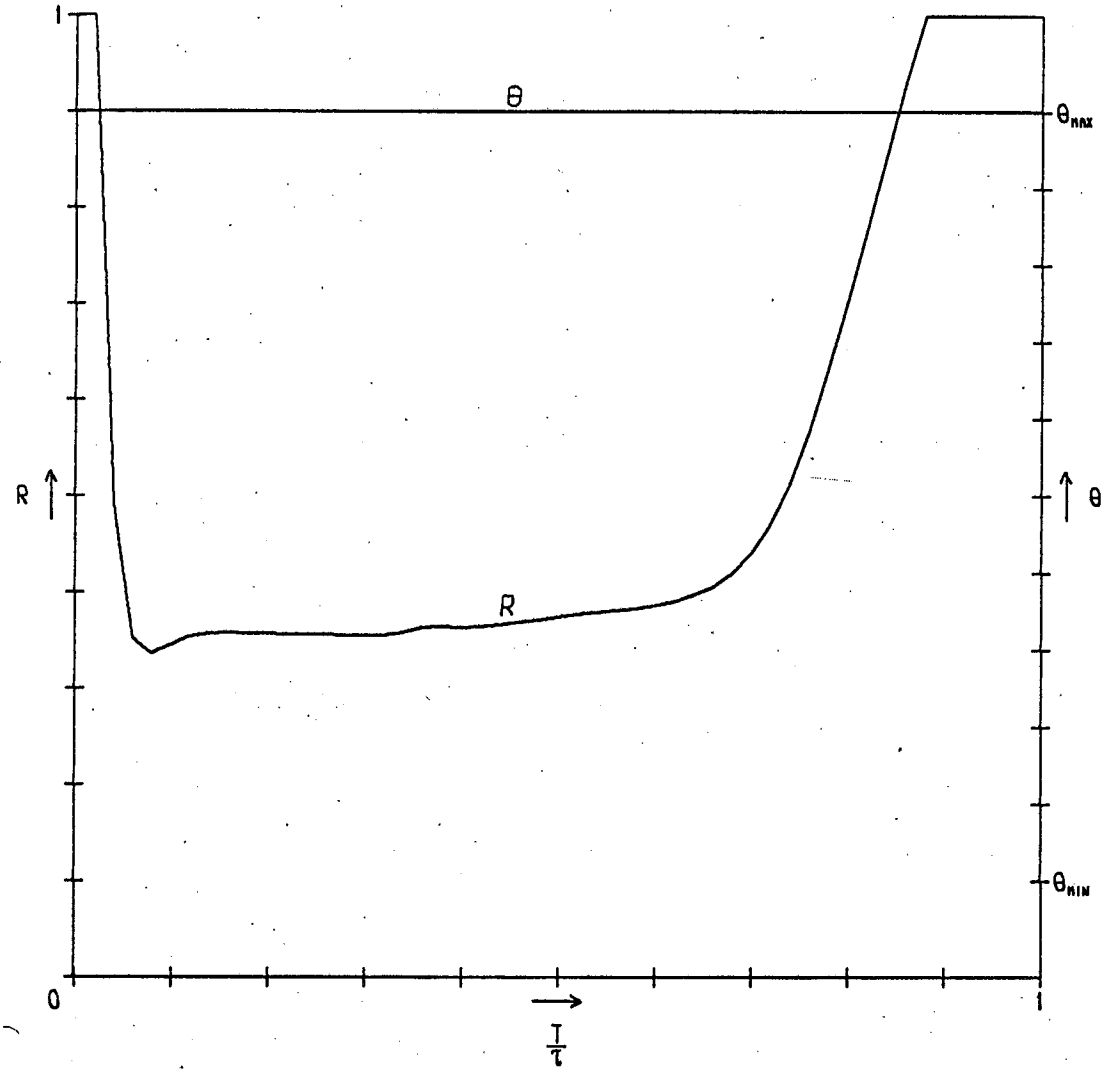
τ = 4.0000

$K_1 = 6.1610 \times 10^3 \, EXP(-5000/T)$

$K_2 = 9.6719 \times 10^5 \, EXP(-7500/T)$

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.626



Graph 5.5

Control policies obtained by the method of Gradients in Function Space for E_2/E_1 = 1.5 .

R_0 = 1.0000

R_{max} = 1.0000

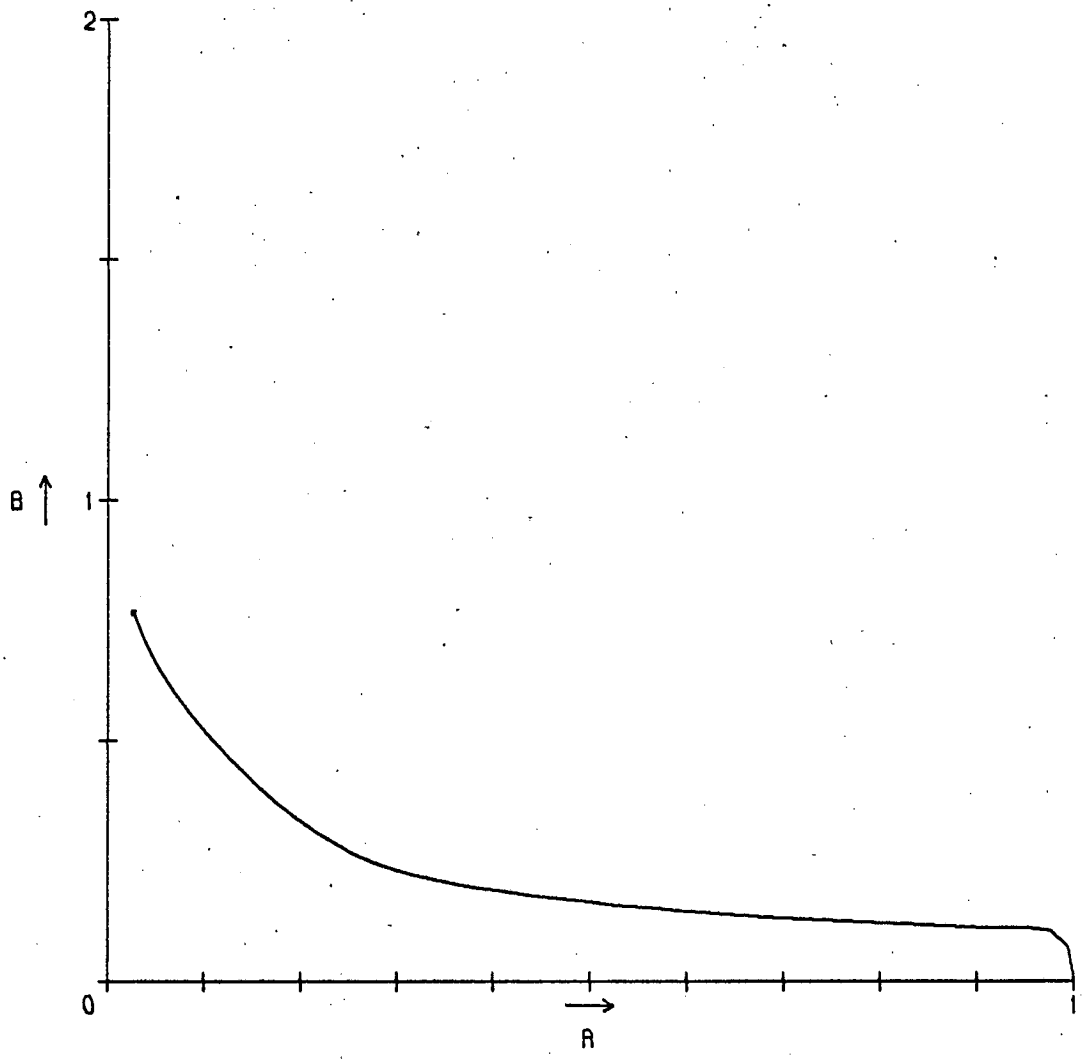
τ = 4.0000

$K_1 = 6.1610 \times 10^3 \exp(-5000/T)$

$K_2 = 9.6719 \times 10^5 \exp(-7500/T)$

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.626



Graph 5.6

Solution trajectory in the a-b plane for the control policies of Graph 5.5 .

R_0 = 1.0000

R_{max} = 1.0000

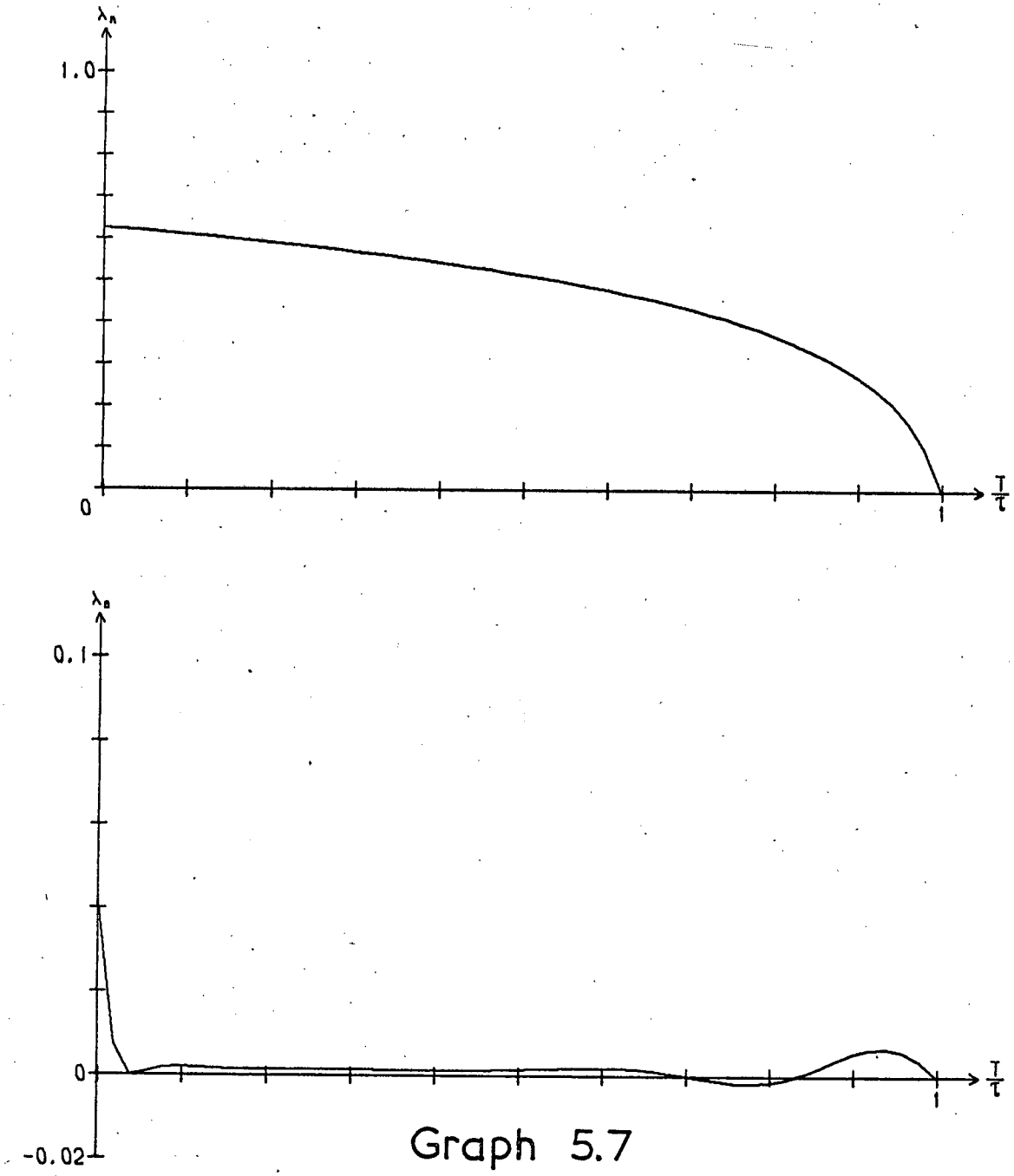
τ = 4.0000

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 9.6719 x 10^5 EXP(-7500/T)

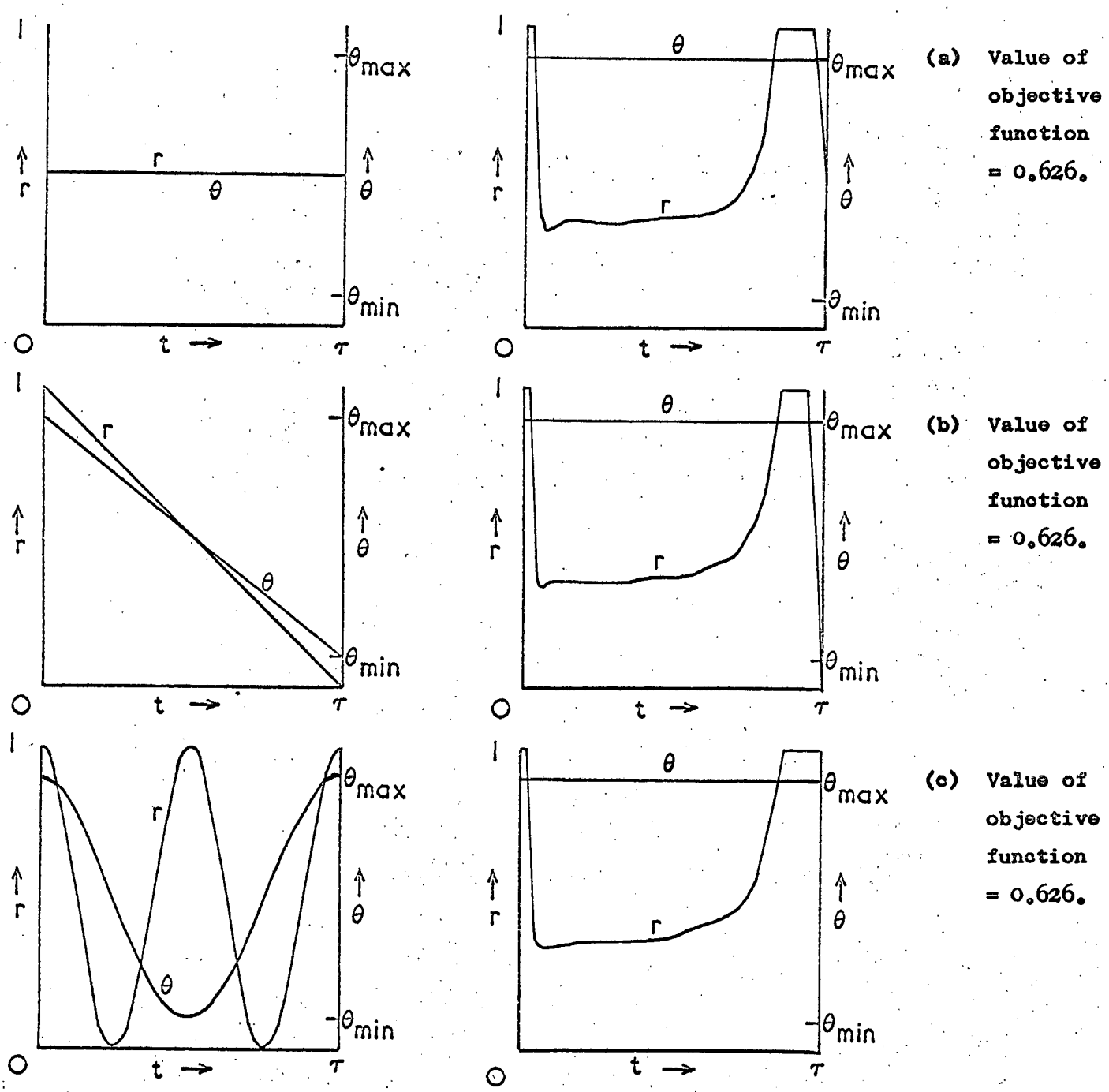
TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.626



Graph 5.7

Adjoint variables for the control policies of Graph 5.5 .



Graph 5.8

Graphs of different initial and resultant final control profiles for Gradient in Function Space searches for the optimal addition-rate and temperature policies. $a_o = 1$, $k_1 = 1$ and $k_2 = 2$ at 300°C, $\theta_{min} = 250°C$, $\theta_{max} = 350°C$, $r_{max} = 1$, $E_1 = 5000$, $E_2 = 7500$ and batch time $\tau = 4$.

R_0 = 1.0000

R_{max} = 1.0000

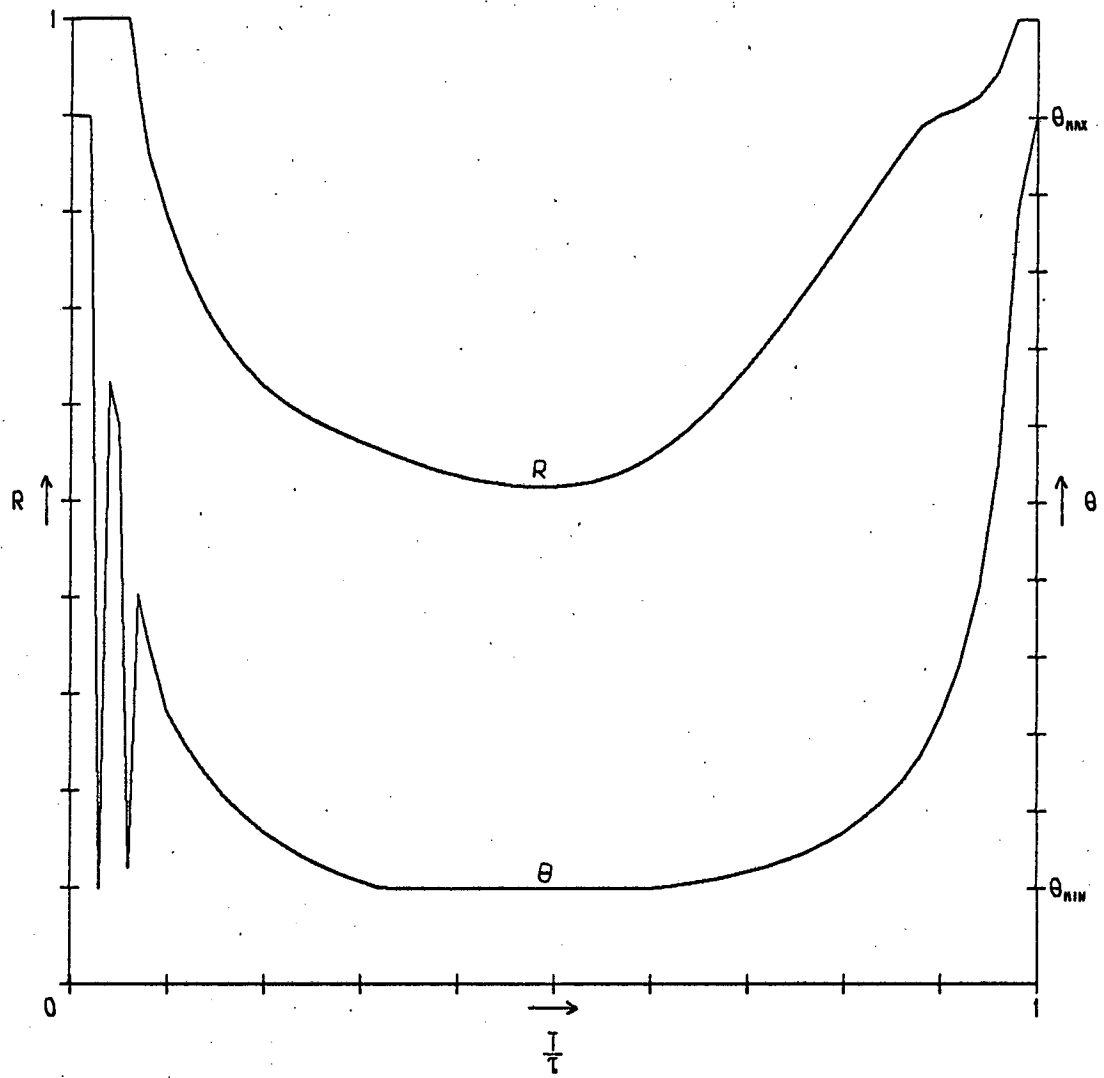
τ = 4.0000

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 1.8168 x 10^6 EXP(-10500/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.582



Graph 5.9

Control policies obtained by the method of Gradients in Function Space for E_2/E_1 = 2.1 .

A_0 = 1.0000

R_{max} = 1.0000

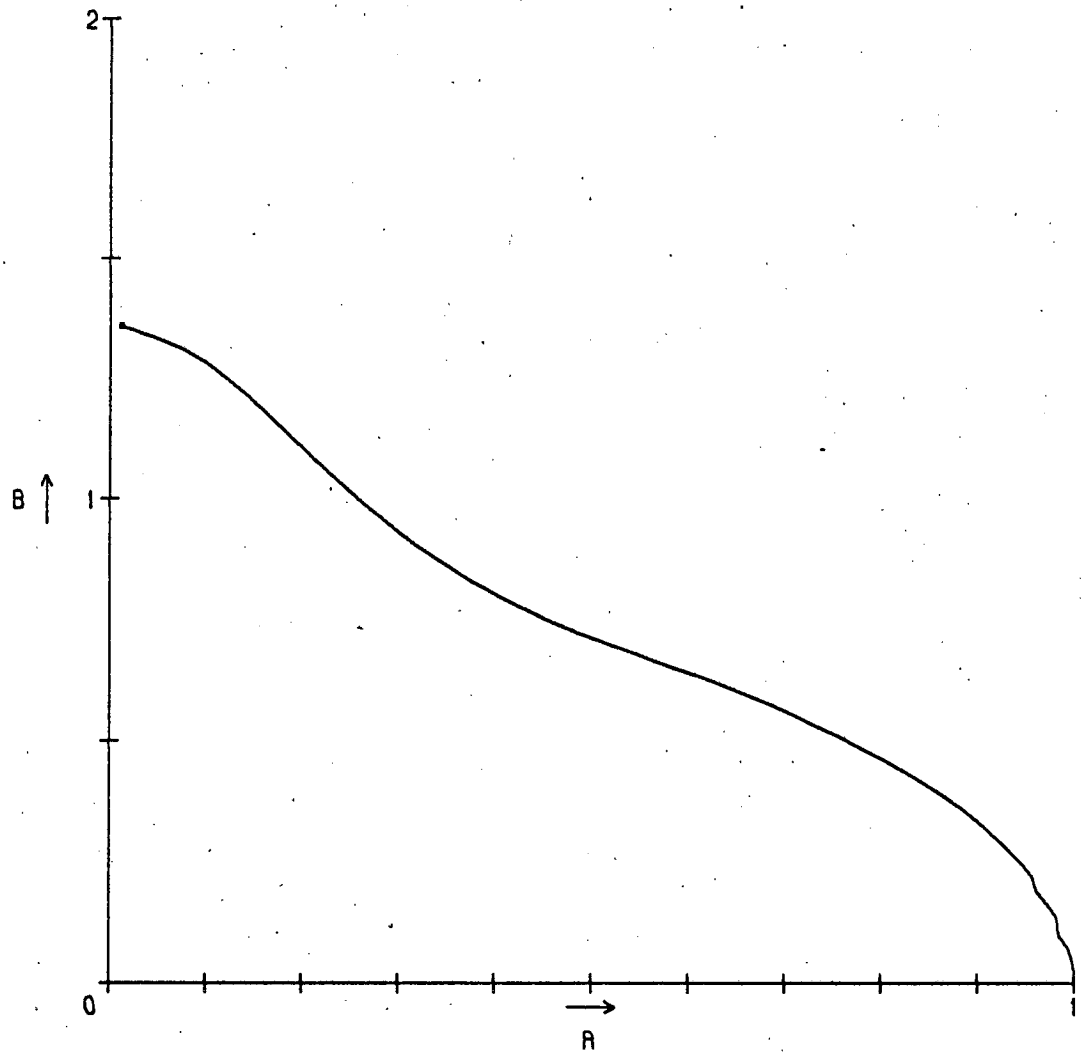
τ = 4.0000

$K_1 = 6.1610 \times 10^3 \exp(-5000/T)$

$K_2 = 1.8168 \times 10^6 \exp(-10500/T)$

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - $C(\tau)$ = 0.582



Graph 5.10

Solution trajectory in the a-b plane for the control policies of Graph 5.9 .

A_0 = 1.0000

R_{max} = 1.0000

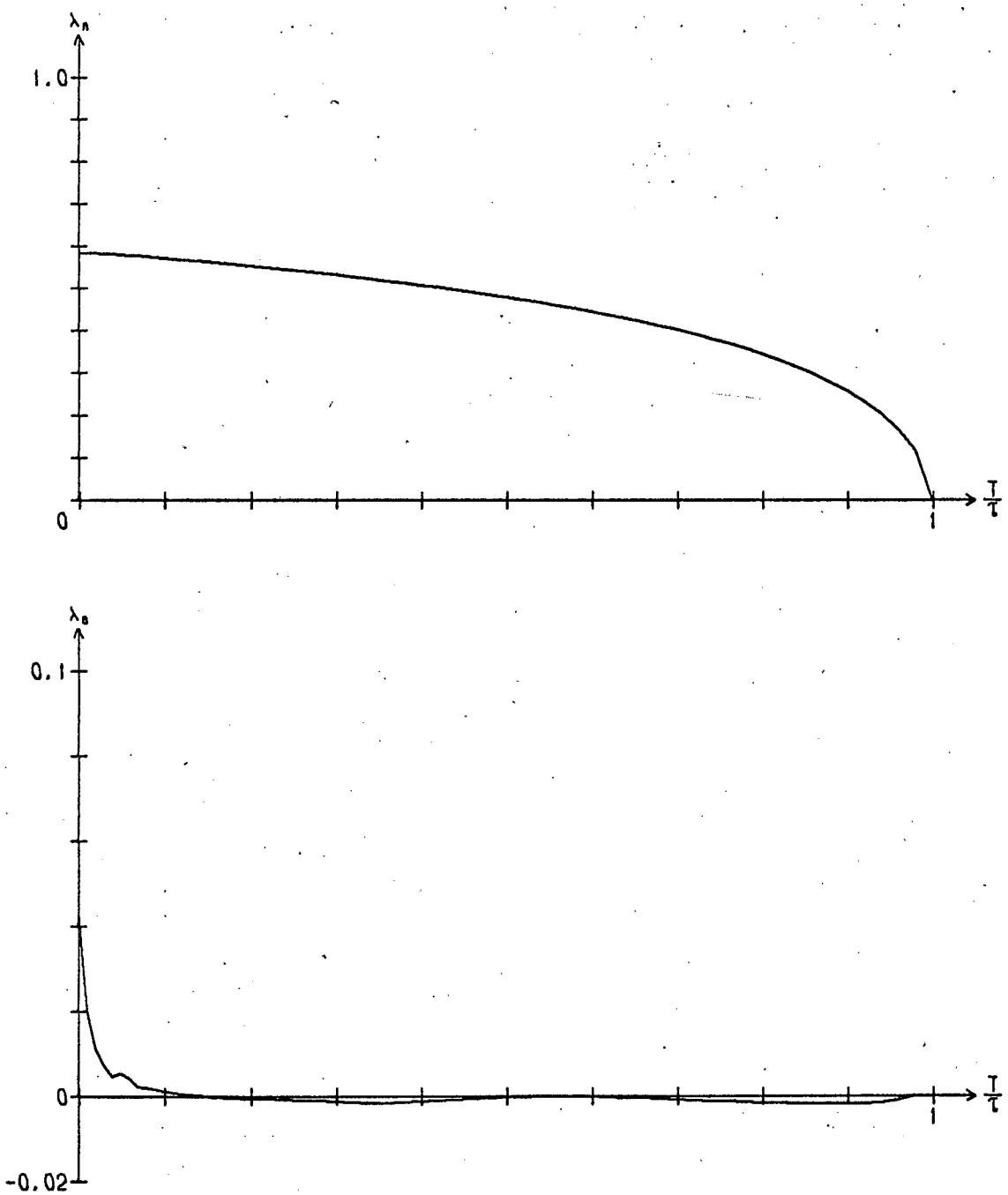
τ = 4.0000

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 1.8168 x 10^8 EXP(-10500/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.582

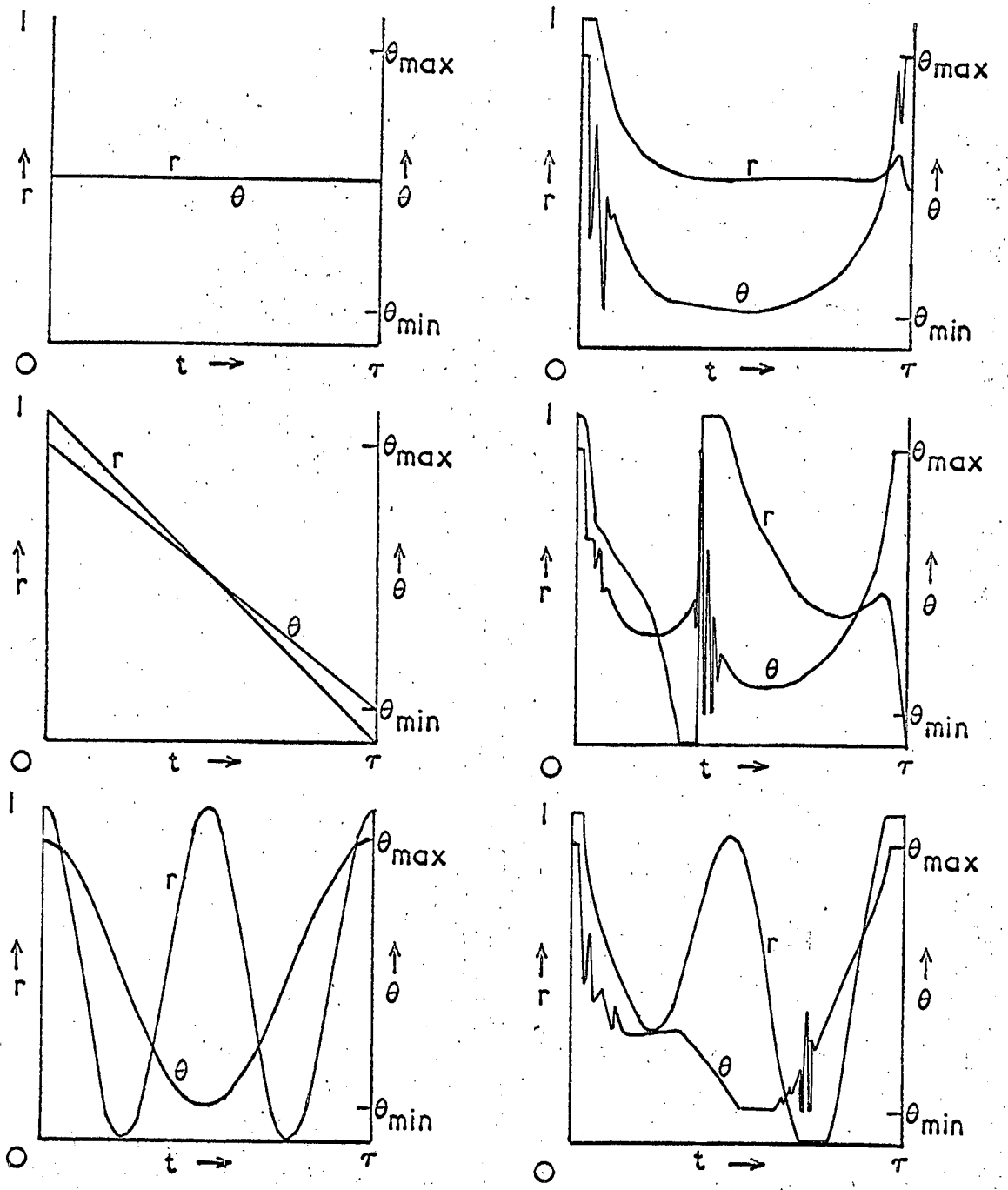


Graph 5.11

Adjoint variables for the control policies of Graph 5.9 .

initial profiles

final profiles



(a) Value of objective function = 0.580.

(b) Value of objective function = 0.574.

(c) Value of objective function = 0.577.

Graph 5.12

Graphs of different initial and resultant final control profiles for Gradient in Function Space searches for the optimal addition-rate and temperature policies. $a_o = 1$, $k_1 = 1$ and $k_2 = 2$ at 300°C, $\theta_{min} = 250°C$, $\theta_{max} = 350°C$, $r_{max} = 1$, $E_1 = 5000$, $E_2 = 10500$ and batch time $\tau = 4$.

R_0 = 1.0000

R_{max} = 1.0000

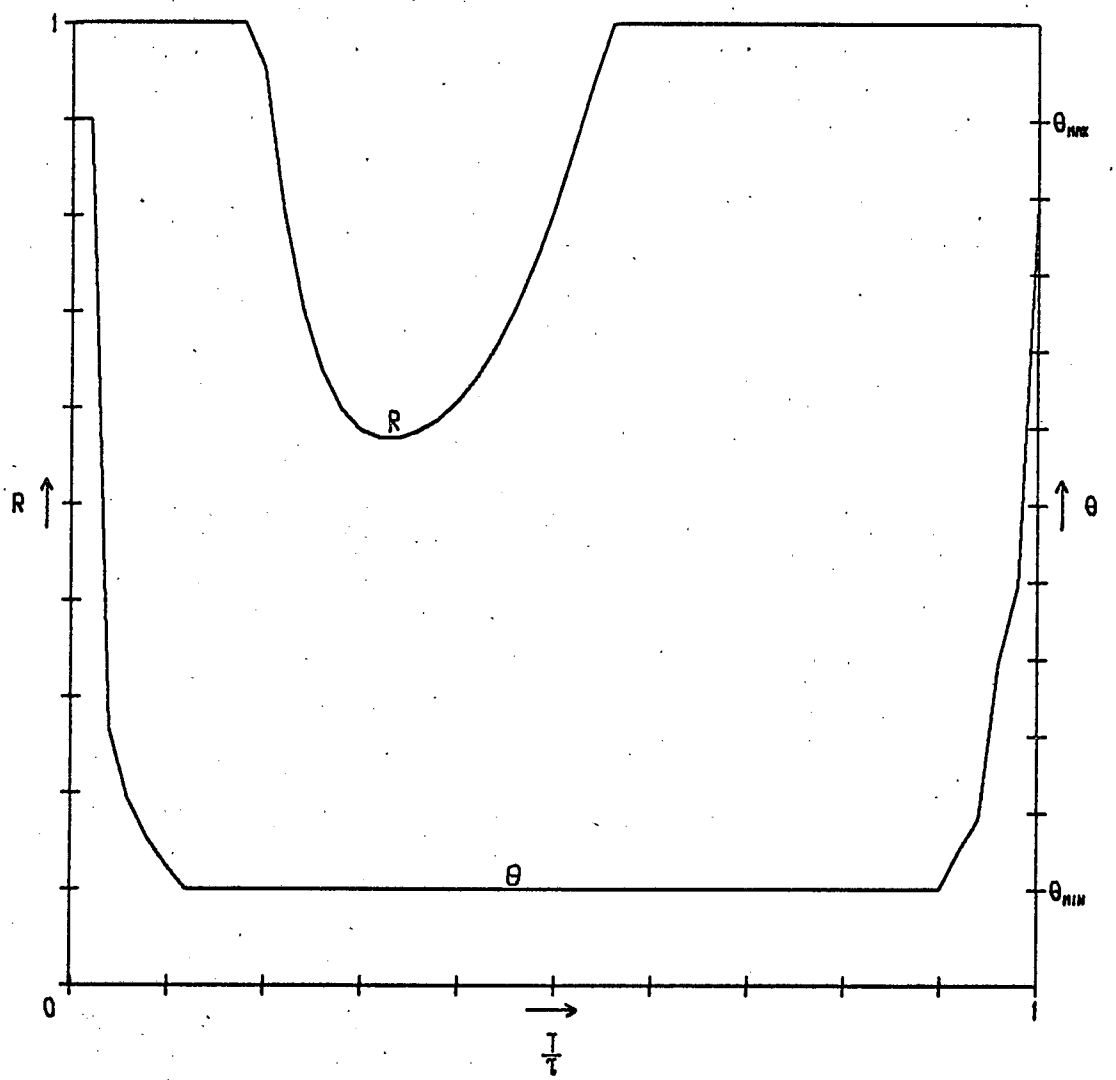
τ = 4.0000

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 4.6773 x 10^{11}EXP(-15000/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.686



Graph 5.13

Control policies obtained by the method of Gradients in Function Space for E_2/E_1 = 3.0 .

A_0 = 1.0000

R_{max} = 1.0000

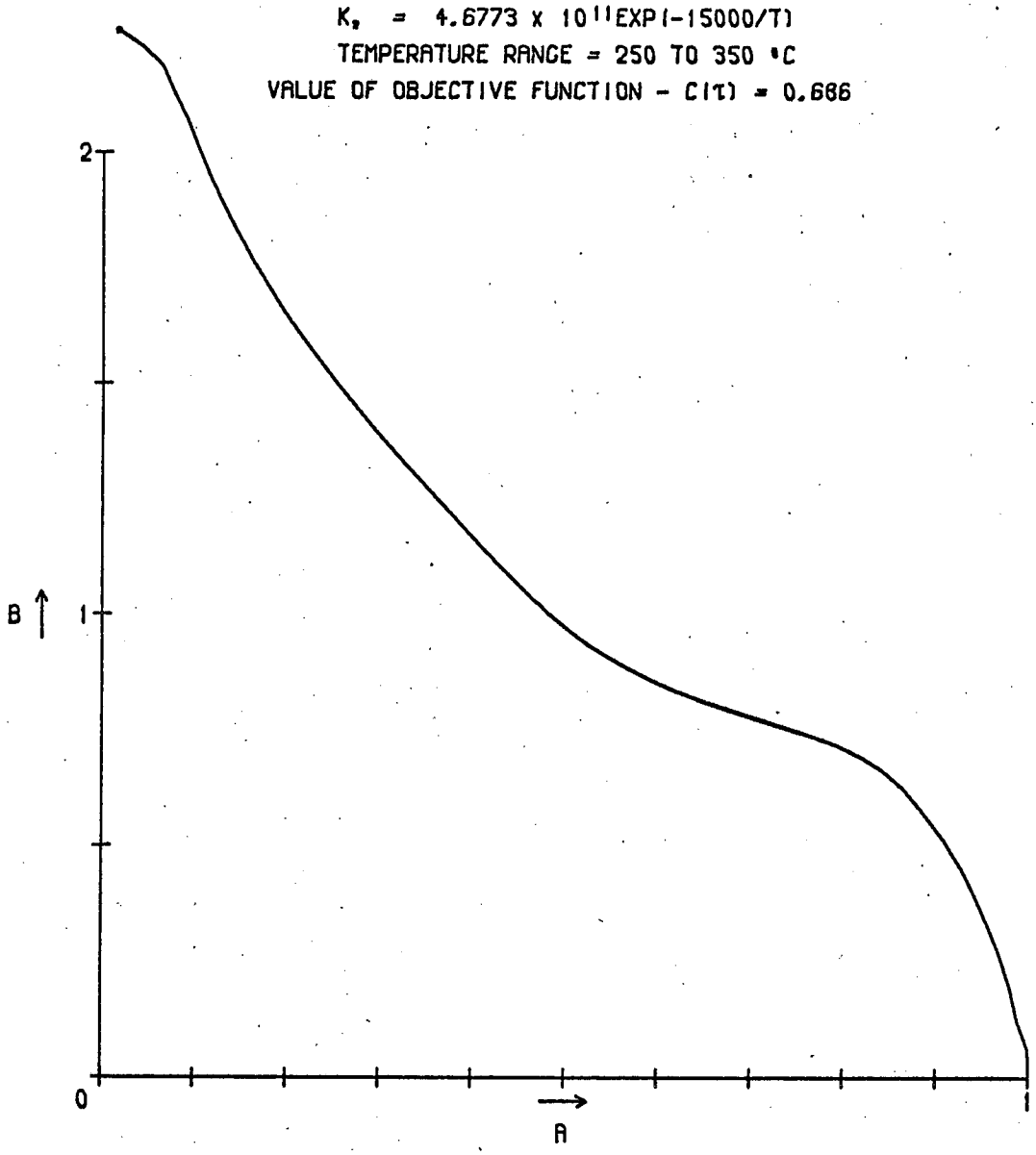
τ = 4.0000

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 4.6773 x 10^{11}EXP(-15000/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.686



Graph 5.14

Solution trajectory in the a-b plane for the control policies of Graph 5.13 .

A_0 = 1.0000

R_{max} = 1.0000

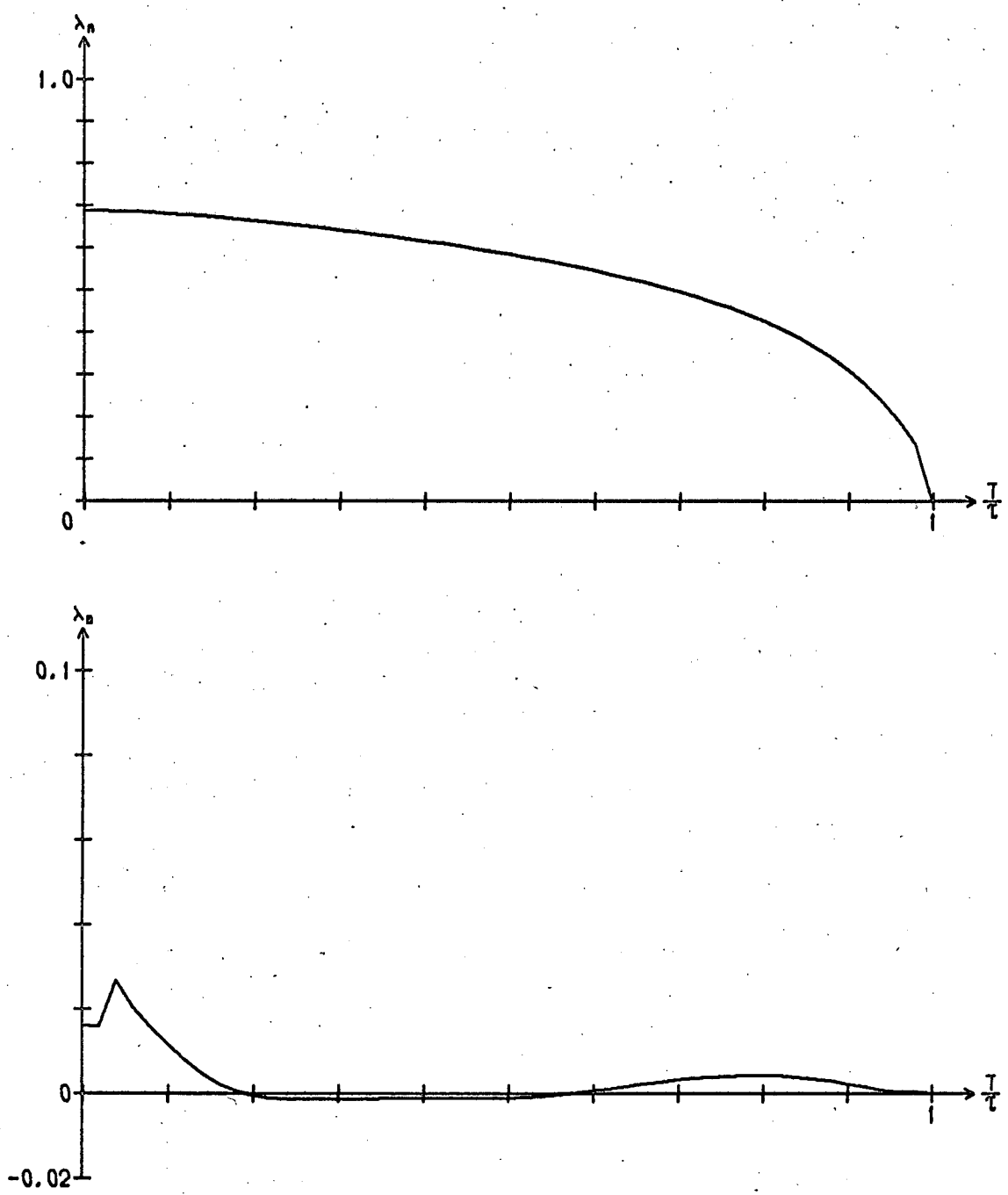
τ = 4.0000

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 4.6773 x 10^{11}EXP(-15000/T)

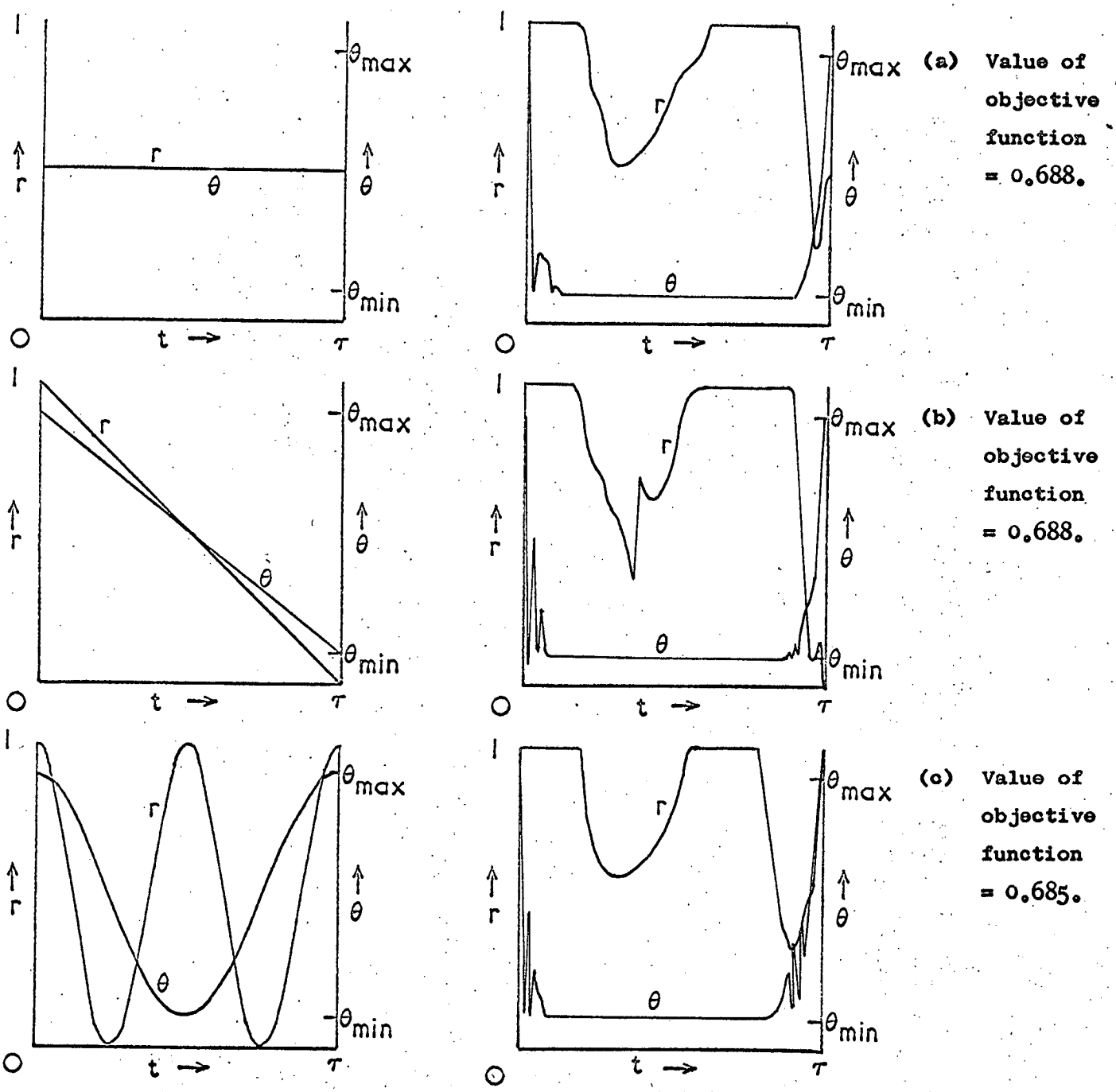
TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.686



Graph 5.15

Adjoint variables for the control policies of Graph 5.13 .



Graph 5.16

Graphs of different initial and resultant final control profiles for Gradients in Function Space searches for the optimal addition-rate and temperature policies. $a_o = 1$, $k_1 = 1$ and $k_2 = 2$ at $300^{\circ}C$, $\theta_{min} = 250^{\circ}C$, $\theta_{max} = 350^{\circ}C$, $r_{max} = 1$, $E_1 = 5000$, $E_2 = 15000$ and batch time $\tau = 4$.

problem by a Gradients in Function Space method. In this latter case the exact profile {47} has discontinuities.

As a check that these profiles are optimal, a number of searches were made with different initial profiles for θ and r for each of the sets of activation energies mentioned above. These initial profiles and the resultant final controls are shown for $E_2 = 0.9E_1$, $E_2 = 1.5E_1$, $E_2 = 2.1E_1$ and $E_2 = 3E_1$ in Graphs 5.4, 5.8, 5.12 and 5.16 respectively, and it is seen that, except for $E_2 = 2.1E_1$, the profiles are similar in shape to those obtained in the corresponding original searches. The values of the objective functions are not in as close agreement for $E_2 > 2E_1$ as they were in similar searches in the isothermal control of Chapter 3. This probably results from the convergence becoming very slow towards the end for some of the searches. Oscillations in the temperature profile, similar to those of Graph 5.9, are again seen to appear in some cases, particularly for $E_2 = 2.1E_1$.

For $E_2 = 2.1E_1$ the final profiles for different initial profiles are considerably different, and wild oscillations, particularly in the temperature profile, tend to occur. These difficulties probably arise from the ratio of the activation energies $\frac{E_2}{E_1}$ being close to 2, the value at which the form of the optimal temperature profile changes considerably. The form of the gradient function for temperature for any initial profile must also change when $\frac{E_2}{E_1}$ passes through 2, and at values of this ratio of activation energies close to 2 the effect of temperature changes will be small. It is well known in simple gradient methods of searching for maxima of functions of a finite number of variables that, if the gradient is small in value, convergence is slow and can almost

cease at a point far removed from the true optimum. The eventual point taken as the optimum then often depends on the starting point. In a similar way it appears that poor convergence is being obtained for searches with $E_2 = 2.1E_1$, particularly as the values of the objective function obtained differ quite largely.

For $E_2 = 3E_1$, however, the differences in the control profiles and in the values of the objective function for different initial profiles are less marked, indicating that the gradient function for temperature has larger values than for $E_2 = 2.1E_1$. However, the differences are still greater than those observed in Chapter 3 when the rate of addition was the only control, and it appears therefore that this problem of convergence due to the relatively small effect of temperature is still present.

From the results of these searches it can be concluded that the profiles obtained are approximations to the true optimal controls. The three segment rate of addition control suggested previously appears to be confirmed. The optimal temperature control for $E_2 < 2E_1$ is evidently $\theta = \theta_{max}$ throughout, whereas for $E_2 > 2E_1$ the temperature is not constant during the batch time, changing from θ_{max} to θ_{min} for some period during the initial non-singular segment, and from θ_{min} to θ_{max} during the final non-singular segment. It has already been shown that θ cannot switch instantaneously from one limit to the other on an optimal profile, and therefore the temperature must change continuously between its limits during the non-singular segments for these relative values of the activation energies.

It would appear from Graph 5.13 that this section of intermediate

θ does not extend for the full duration of the non-singular segments, and thus $\theta = \theta_{min}$ for finite periods at the end of the initial segment and at the beginning of the final segment. This is less clear from Graph 5.9.

These Gradient in Function Space calculations give some useful confirmations of the form of the optimal profile, and there is now sufficient information to enable an attack on an exact calculation of the optimal trajectory to be made.

5.1.4 Exact Solution

The general philosophy of the calculation procedures used in the previous examples is followed to evaluate the profile of r, but in detail certain modifications must be made to take account of the required temperature profile for $E_2 > 2E_1$.

On the section of intermediate θ, $\frac{\partial H}{\partial \theta}$ is zero, and during the calculation of the non-singular segments this condition is used to determine at what point these sections start. However, evaluation of $\frac{\partial H}{\partial \theta}$ by equation (5.14) requires knowledge of the values of the adjoint variables. While these are available on the final segment, they are not calculated until after the determination of the state variable profiles in the initial segment. In the integration of the final segment, therefore, in order to find when the section of intermediate temperature starts, it is necessary only to evaluate $\frac{\partial H}{\partial \theta}$ and find when it reaches zero. When this occurs the value of θ at each point is then chosen to keep $\frac{\partial H}{\partial \theta}$ zero until θ reaches its other limit.

In the evaluation of the initial segment in previous problems the adjoint equations were not integrated with the state equations since the initial values of the adjoint variables are not known. The adjoint variables could only be found after evaluation of the state variable profiles on the initial segment by integration backwards from the point of intersection of the initial and singular segments, using the known values of the adjoint variables at this point on the singular segment. In this problem, however, forward integration of the state variables along the initial segment is not feasible because knowledge of the adjoint variables is required for evaluation of the temperature profile. It is therefore necessary to integrate state and adjoint variables backwards from the intersection of the initial and singular segments. This is done by guessing at, say, the value of a at this intersection, calculating the values of b and λ_a at this point ($\lambda_b = 0$) and integrating backwards along the initial segment with $r = r_{max}$. $\frac{\partial H}{\partial \theta}$ is calculated at each point along this segment and the section of intermediate θ found as described for the final segment. When the value of b reaches zero the point $t = 0$ has been reached, and the value of a gives the starting concentration of A for the initial segment. In general this value will not be equal to a_o, and so adjustment of the guess at the concentration of A at the end of the initial segment is required so that the calculated value of a at $t = 0$ matches up with the desired value, a_o.

For $E_2 > 2E_1$, the value of θ is set to θ_{min} before starting the integrations of the initial and final segments as described above. For $E_2 < 2E_1$, the same method of evaluation of these segments can be used, with of course θ set to θ_{max} for each non-singular segment before

evaluation commences. Evaluation of $\frac{\partial H}{\partial \theta}$ at each point then serves as a check that the optimal policy for θ is θ_{max} throughout, as indicated in the Gradients in Function Space solutions. Although the converse of the derivation of equation (5.27), that discontinuous changes in θ satisfy the maximum principle for $E_2 < E_1$, is not universally true, it is still possible that discontinuous switching of θ could occur, and so evaluation of $\frac{\partial H}{\partial \theta}$ should be made at both θ_{min} and θ_{max} for calculations with $E_2 < E_1$.

The singular segment is calculated in exactly the same way as previously, with $\theta = \theta_{max}$ or θ_{min} for $E_2 < 2E_1$ and $E_2 > 2E_1$ respectively. The full calculation procedure is described in flow-diagram form in Appendix II.

Trajectories obtained by such exact calculations are shown in Graphs 5.17 to 5.19 for $E_2 = 1.5E_1$, where it is seen that the solution control for θ is $\theta = \theta_{max}$ throughout, as anticipated. For $E_2 > 2E_1$, this form of temperature control is no longer optimal, as is shown in Graphs 5.20 to 5.22 for $E_2 = 2.1E_1$, and in Graphs 5.23 to 5.25 for $E_2 = 3E_1$, and the expected temperature profiles are obtained.

It is now easy to show that the Hamiltonian shows a maximum value on the sections of the trajectory where θ varies. Differentiation of equation (5.14) with respect to θ gives

$$\frac{\partial^2 H}{\partial \theta^2} = \frac{(E_1 - 2\theta)\frac{\partial H}{\partial \theta} - (E_2 - E_1)k_2 E_2(\lambda_a + 2\lambda_b)}{\theta^4}. \qquad (5.30)$$

On the sections of intermediate θ, $\frac{\partial H}{\partial \theta}$ is zero, and λ_a and λ_b are both

R_0 = 1.0000

R_{max} = 1.0000

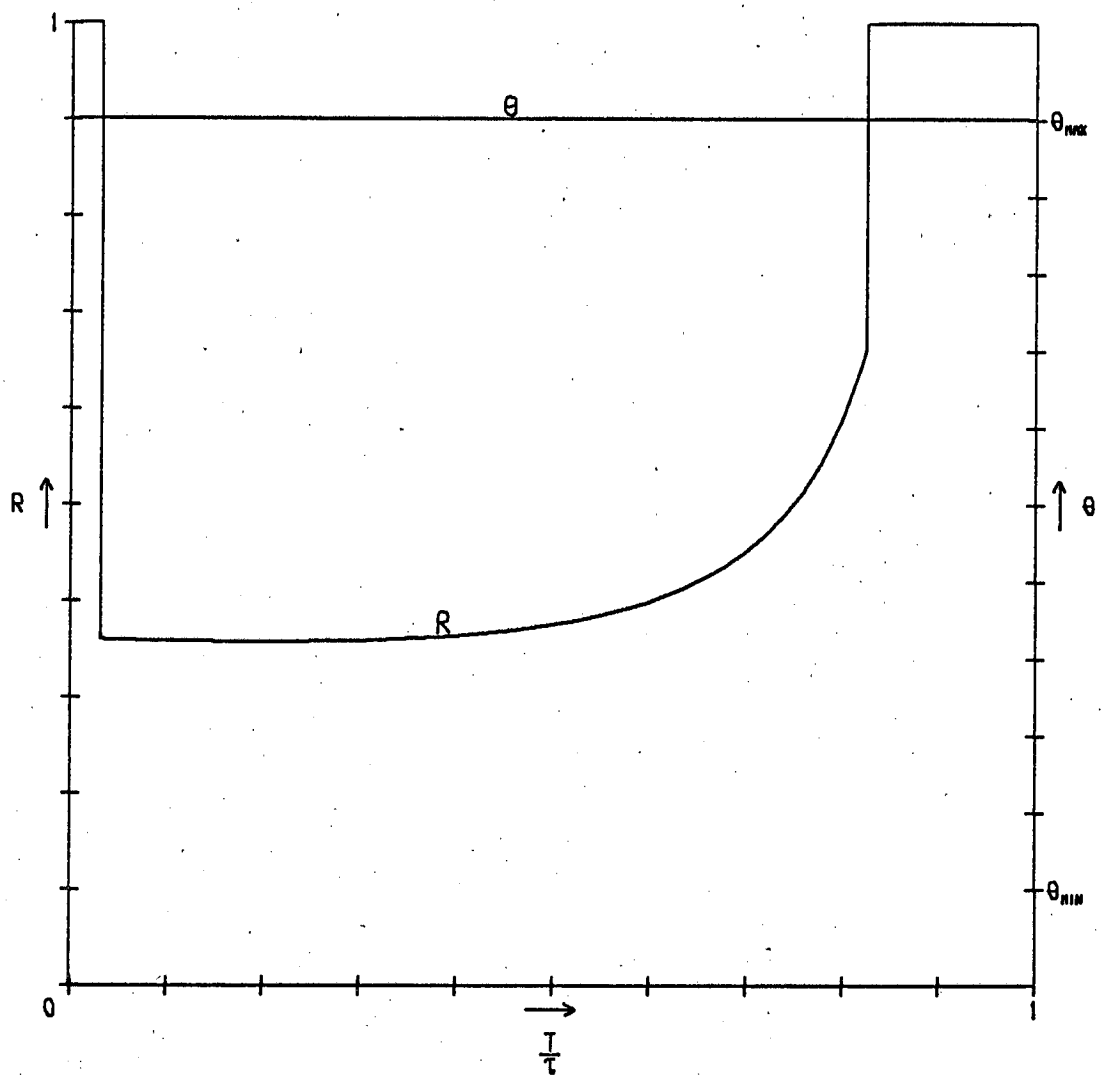
τ = 4.0002

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 9.6719 x 10^5 EXP(-7500/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.6256



Graph 5.17

Exact control policies satisfying the maximum principle for E_2/E_1 = 1.5 .

A_0 = 1.0000

R_{max} = 1.0000

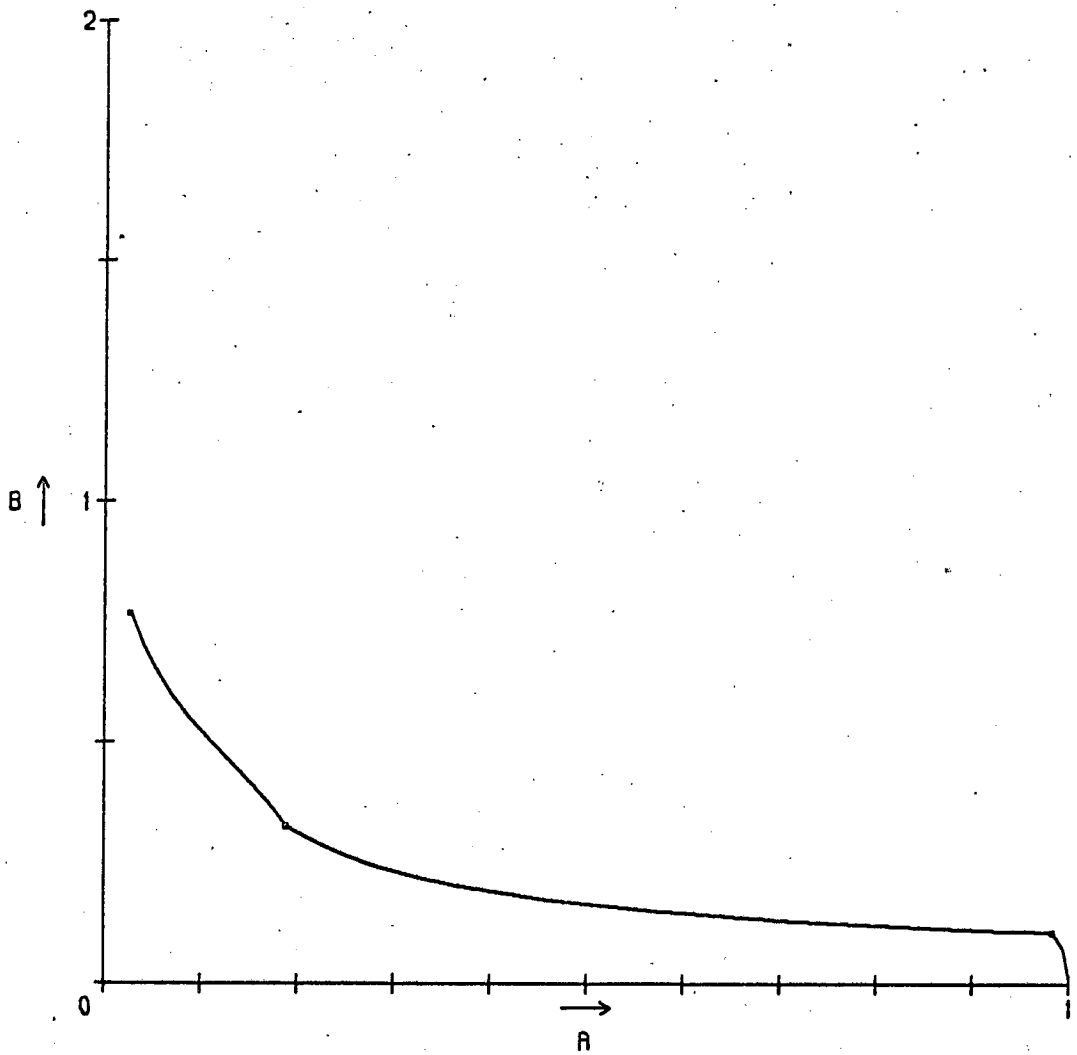
τ = 4.0002

K_1 = 6.1610×10^3 EXP(-5000/T)

K_2 = 9.6719×10^5 EXP(-7500/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(T) = 0.6256



Graph 5.18

Solution trajectory in the a-b plane for the control policies of Graph 5.17

A_0 = 1.0000

R_{max} = 1.0000

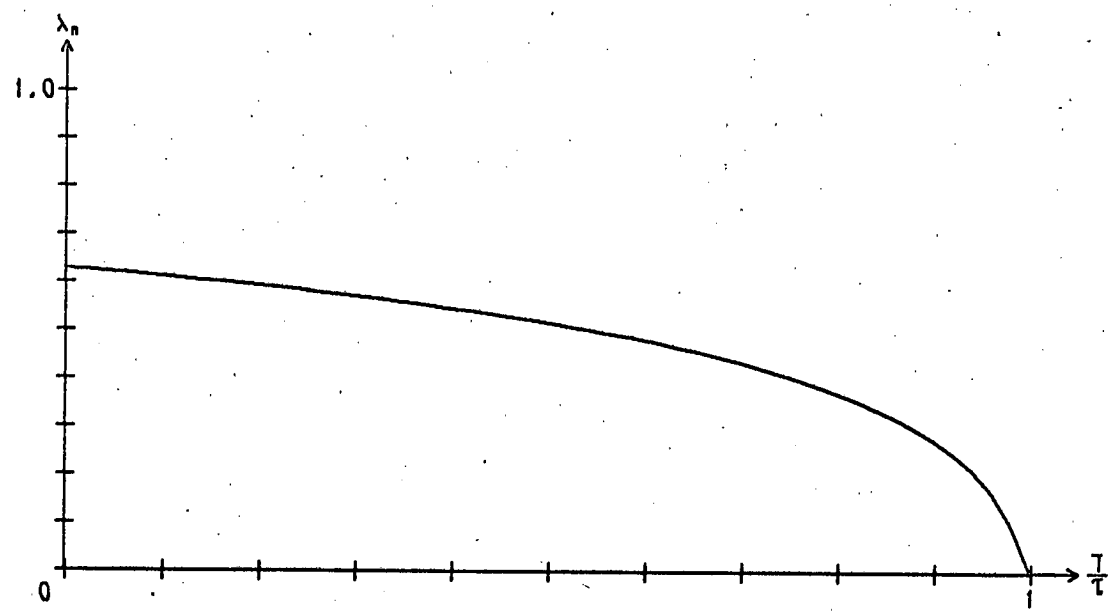
τ = 4.0002

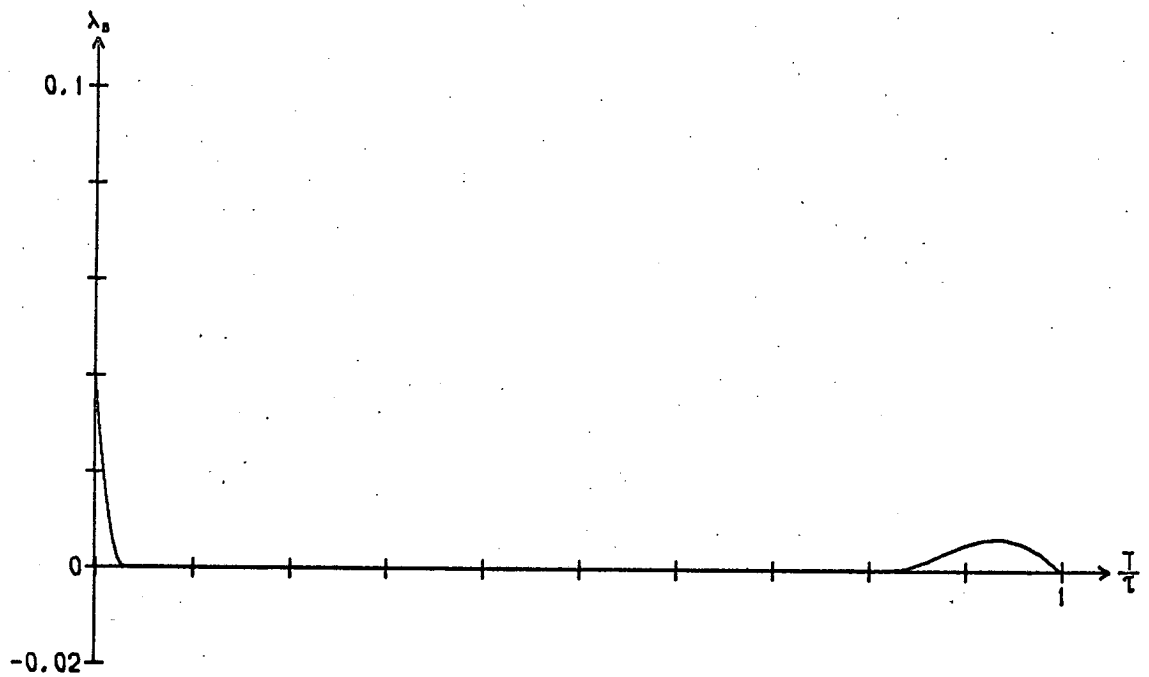
K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 9.6719 x 10^5 EXP(-7500/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.6256





Graph 5.19

Adjoint variables for the control policies of Graph 5.17

R_0 = 1.0000

R_{max} = 1.0000

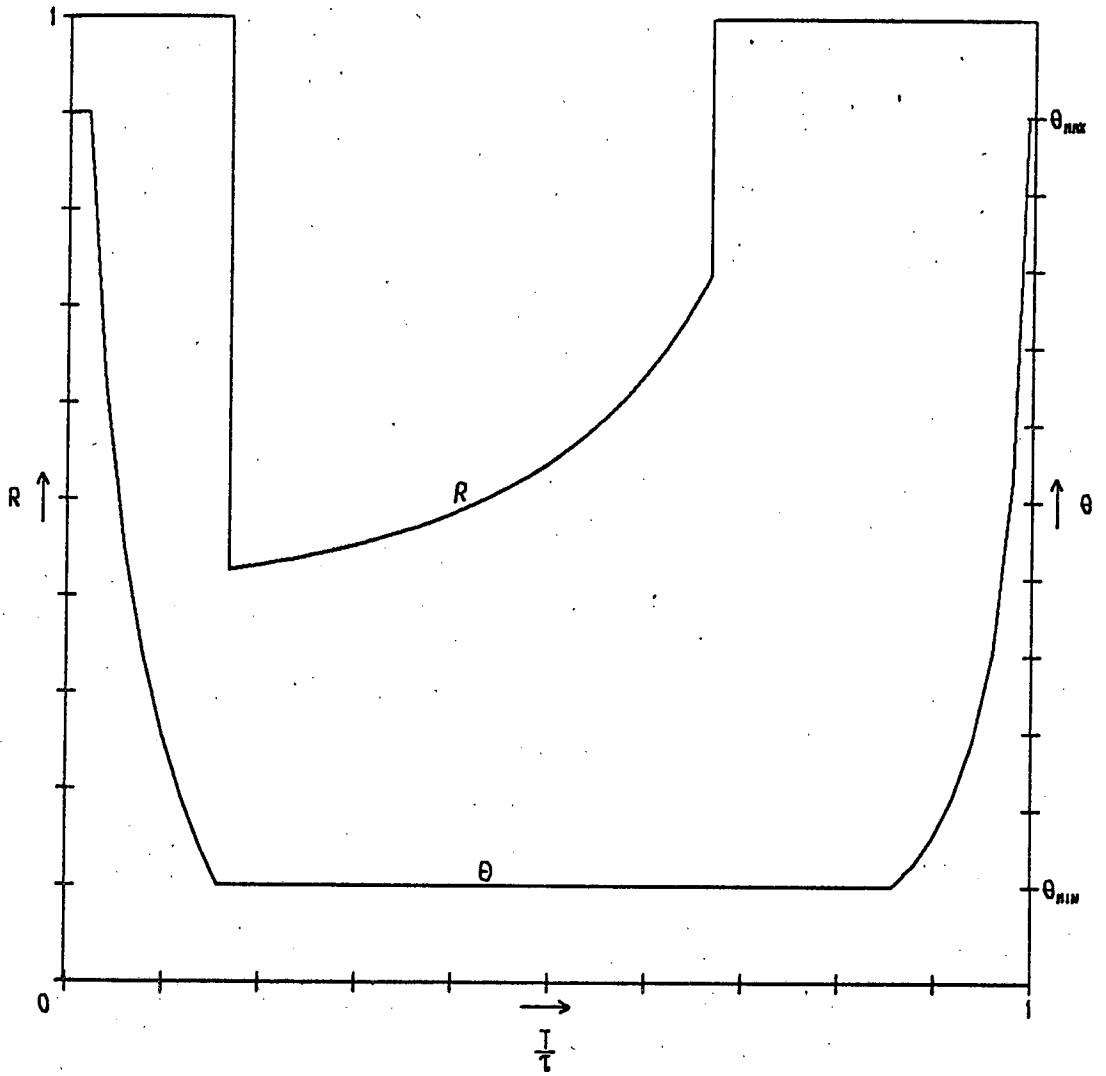
τ = 4.0000

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 1.8168 x 10^8 EXP(-10500/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.5847



Graph 5.20

Exact control policies satisfying the maximum principle for E_2/E_1 = 2.1 .

A_0 = 1.0000

R_{max} = 1.0000

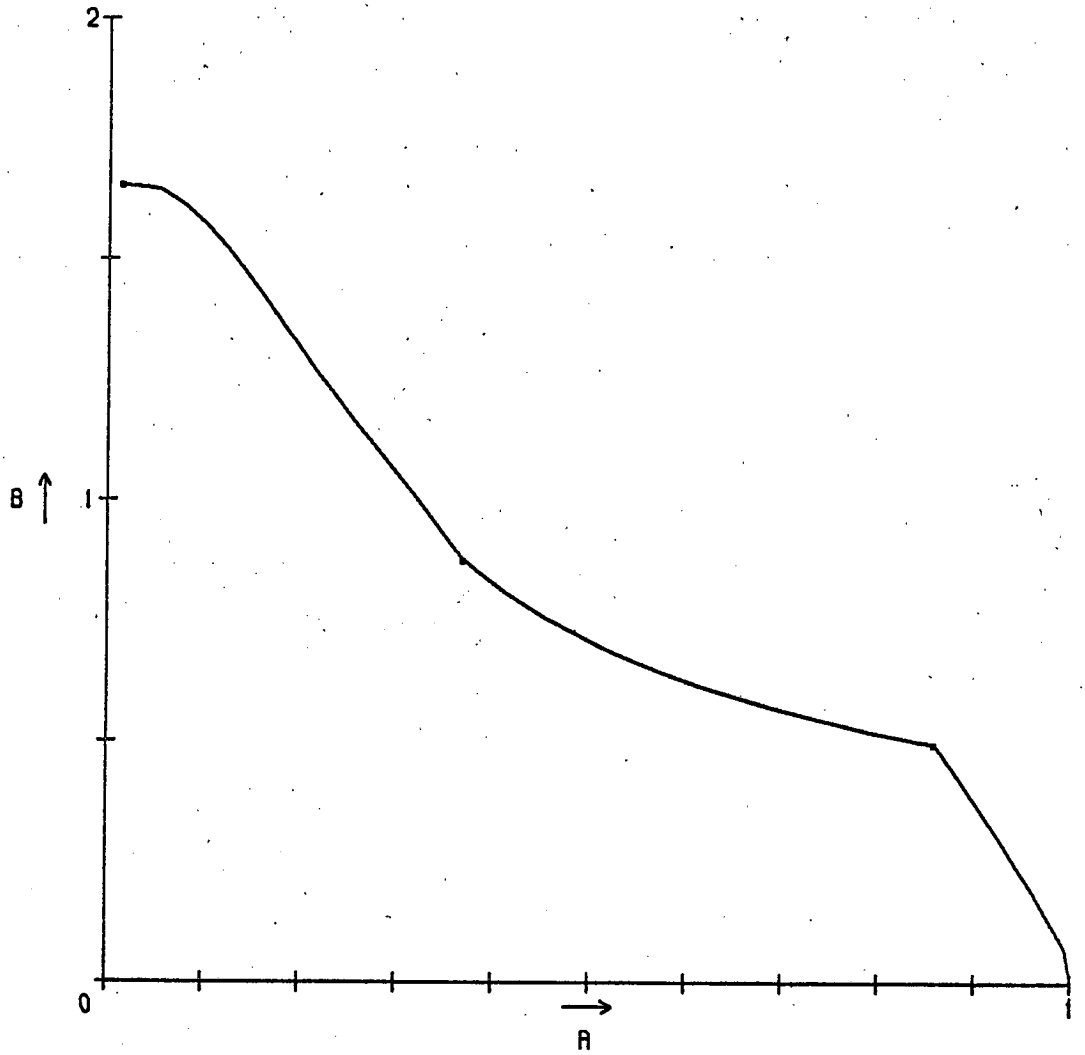
τ = 4.0000

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 1.8168 x 10^6 EXP(-10500/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.5847



Graph 5.21

Solution trajectory in the a-b plane for the control policies of Graph 5.20

$A_0 = 1.0000$

$R_{max} = 1.0000$

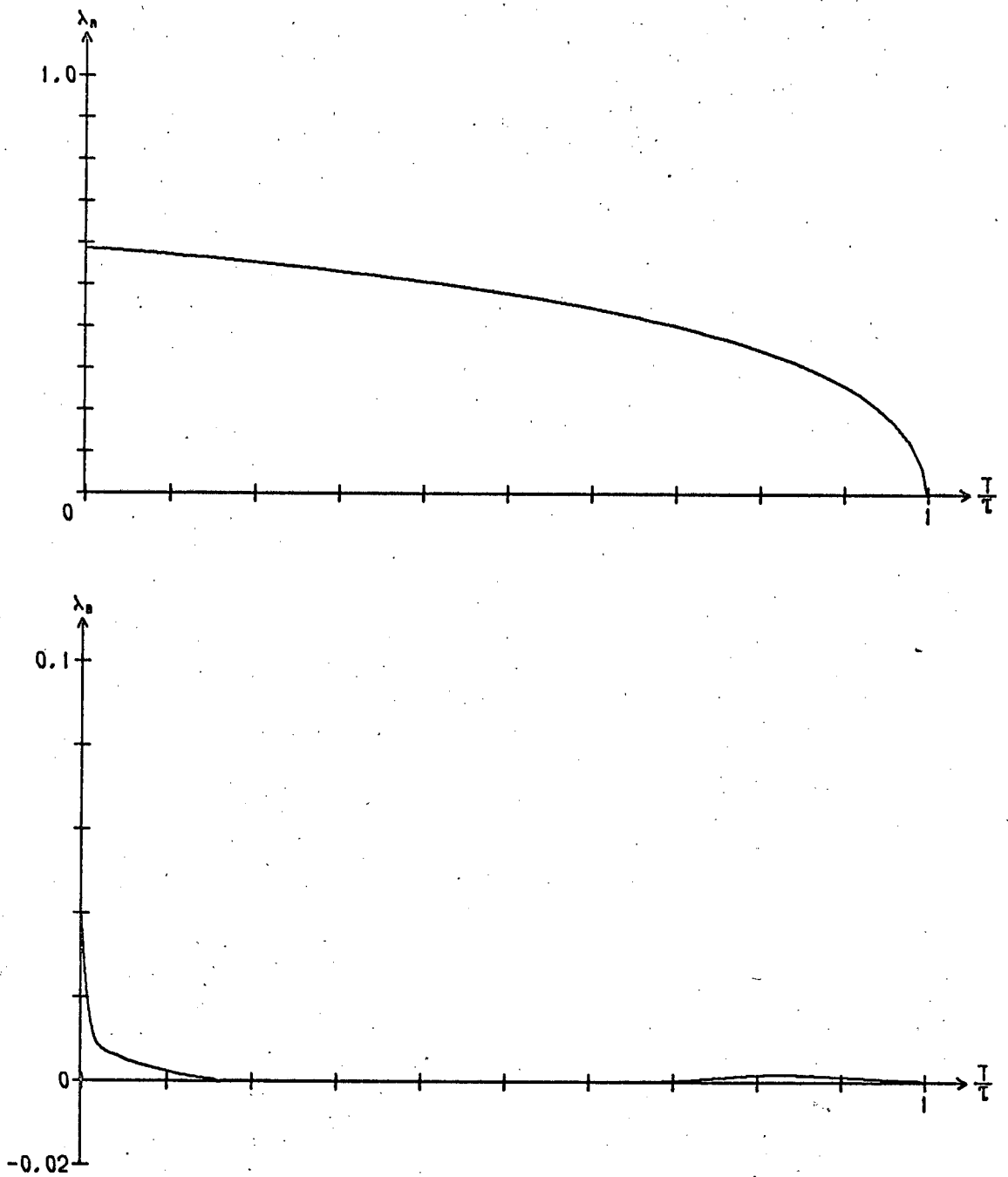
$\tau = 4.0000$

$K_1 = 6.1610 \times 10^3 \, EXP(-5000/T)$

$K_2 = 1.8168 \times 10^6 \, EXP(-10500/T)$

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - $C(\tau) = 0.5847$



Graph 5.22

Adjoint variables for the control policies of Graph 5.20

A_0 = 1.0000

R_{max} = 1.0000

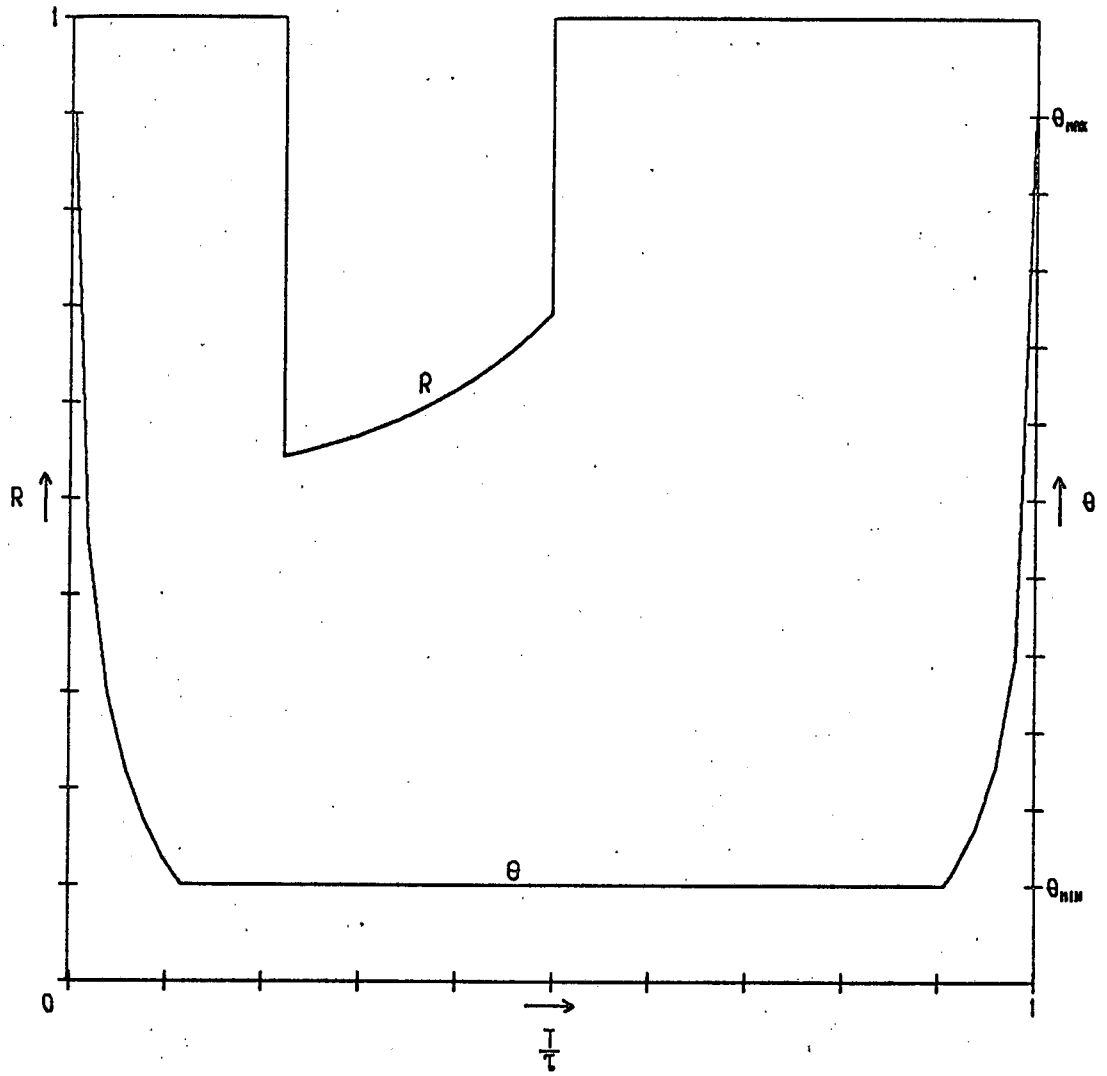
τ = 3.9996

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 4.6773 x 10^{11}EXP(-15000/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.6892



Graph 5.23

Exact control policies satisfying the maximum principle for E_2/E_1 = 3.0 .

A_0 = 1.0000

R_{max} = 1.0000

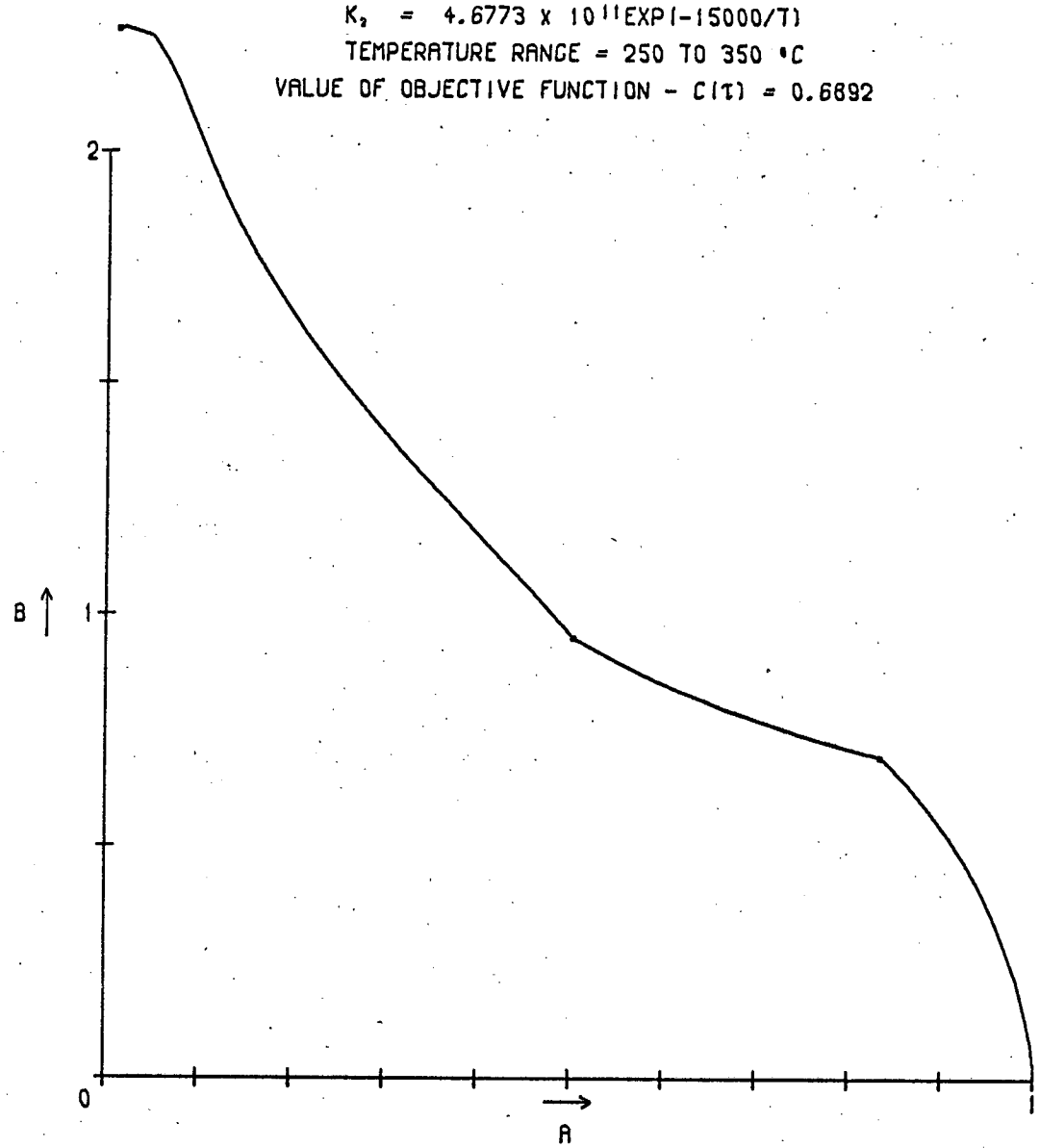
τ = 3.9996

K_1 = 6.1610×10^3 EXP(-5000/T)

K_2 = 4.6773×10^{11}EXP(-15000/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(T) = 0.6892



Graph 5.24

Solution trajectory in the a-b plane for the control policies of Graph 5.23

A_0 = 1.0000

R_{max} = 1.0000

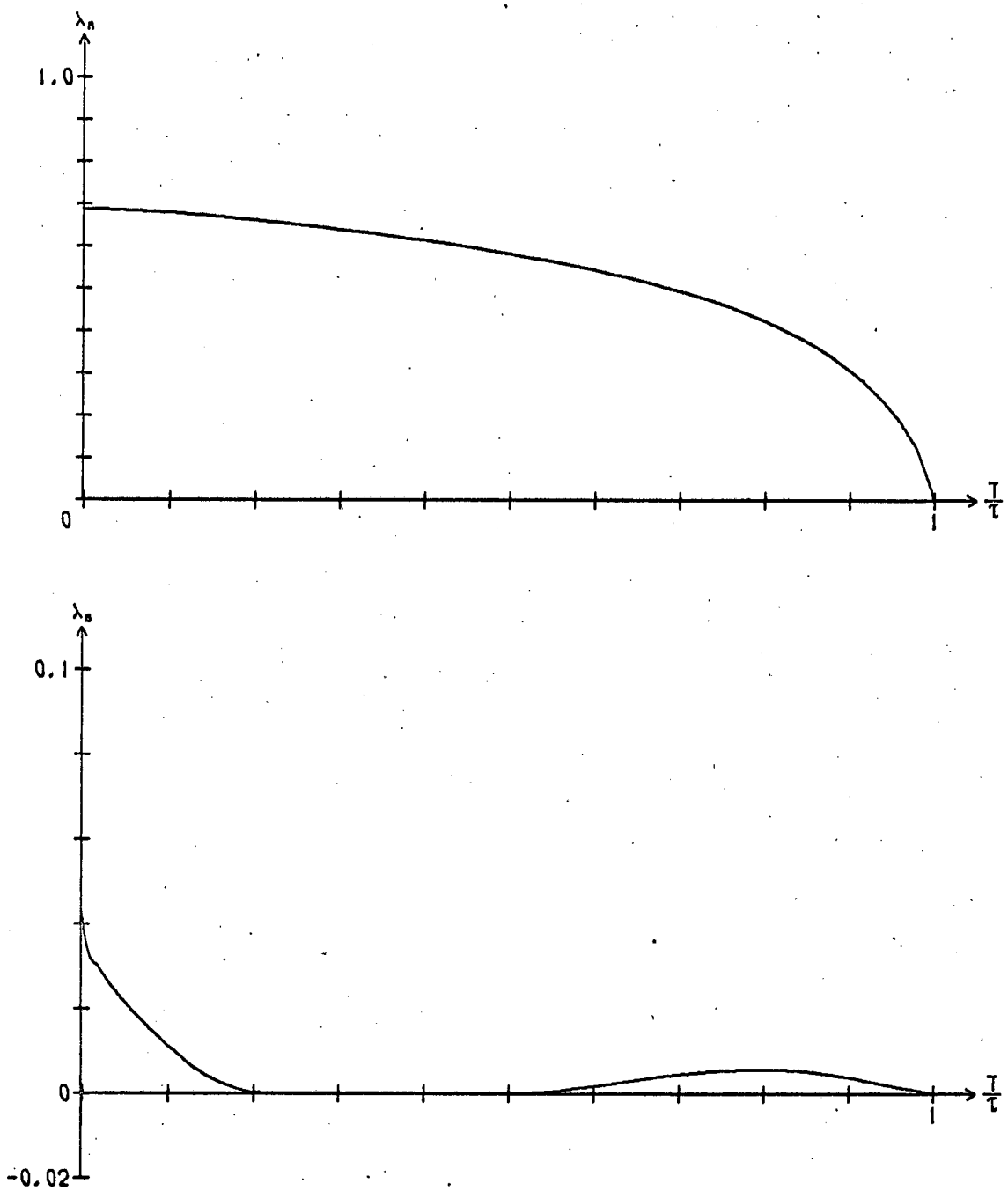
τ = 3.9996

$K_1 = 6.1610 \times 10^3 \, EXP(-5000/T)$

$K_2 = 4.6773 \times 10^{11} EXP(-15000/T)$

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.6692



Graph 5.25

Adjoint variables for the control policies of Graph 5.23

Table 5.1

Comparison of values of the objective function obtained by Gradients in Function Space searches and by exact calculation. $a_o = 1$, $k_1 = 1$ and $k_2 = 2$ at 300^oC, $E_1 = 5000$, $\theta_{max} = 350^oC$, $\theta_{min} = 250^oC$, $r_{max} = 1$ and batch time $\tau = 4$.

$\frac{E_2}{E_1}$	Values of $c(\tau)$ for Gradients in Function Space searches				$c(\tau)$ for exact trajectory evaluation
1.5	0.626	0.626	0.626	0.626	0.6256
2.1	0.582	0.580	0.574	0.577	0.5847
3.0	0.686	0.688	0.688	0.685	0.6892

positive (Graphs 5.22 and 5.25). Thus $\frac{\partial^2 H}{\partial \theta^2}$ is negative, and the Hamiltonian shows a maximum with respect to θ.

The values of the objective function given by these exact calculations are generally close to the corresponding values obtained by the Gradients in Function Space searches with different initial profiles. This comparison is made in Table 5.1, where it is seen that for $E_2 = 1.5E_1$ the difference is within evaluation precision. For $E_2 > 2E_1$ the differences are greater (particularly for $E_2 = 2.1E_1$), and the exact solution gives a greater answer in each case. This suggests that convergence in the Gradients in Function Space searches has not been as good, and the rather large difference in objective function values between the two methods of evaluation for $E_2 = 2.1E_1$ confirms the suspicions expressed previously about the convergence of Gradients in Function Space searches for a value of $\frac{E_2}{E_1}$ so close to 2.

It appears, therefore, that Gradients in Function Space searches

for systems with two independent control variables may not converge as well on the optimal value of the objective function as for systems of a single control variable when these control variables both have non-trivial optimal profiles.

5.2 $E_2 = 2E_1$

Although such exact relative values of activation energies are most unlikely to be found in practice, such a situation deserves a little more investigation since it is only for such relative values of E_1 and E_2 that r and θ can simultaneously take values between their limits.

An equation was derived from the condition that r can take values between its limits (namely $\lambda_b = 0$) for the rate of addition of B (equation (5.18)). For $E_2 = 2E_1$, this equation becomes

$$r = b(k_1 + 2k_2 b)\left(a + \frac{b}{2}\right) - \frac{E_1 b}{\theta^2}\,\frac{d\theta}{dt}\,. \qquad (5.31)$$

In a similar way an equation was derived for the rate of change of temperature for the conditions when θ can take values between its limits (equation (5.24)). Setting $E_2 = 2E_1$ in this equation should give rise to another expression for $\frac{d\theta}{dt}$

$$\frac{d\theta}{dt} = \frac{(b + 2a)(k_1 + 2k_2 b)}{2E_1}\,\theta^2 - \frac{r(t)\theta^2}{E_1 b} \qquad (5.32)$$

which is exactly equivalent to equation (5.31). Thus no further informa-

tion about the behaviour of r and θ on the singular segment is obtained.

The equation of the singular segment in the a - b plane can be derived as previously from the condition of the maximum principle of a constant value of the Hamiltonian, and is given by equation (5.22)

$$k_1(\theta = \theta_{max})N = \frac{k_1 k_2 ab^2}{k_1 + 2k_2 b} .$$

However, this equation has temperature as a variable, since k_1 and k_2 are dependent on temperature (equations (5.3) and (5.4)) and temperature variations are allowed on the singular segment when $E_2 = 2E_1$. Therefore equation (5.22) now represents a family of singular segments, one for each temperature profile. The temperature profile is restricted only in the sense that r and θ are related by equation (5.31) (or, equivalently, (5.32)), and thus there is an infinity of temperature profiles. It follows then that the family of singular segments represented in the a - b plane by equation (5.22) is infinite.

The equation (5.18) for the rate of addition of B on the singular segment and equation (5.22) for the singular segment in the a - b plane were both derived from the condition $\lambda_b = 0$ on the singular segment. It follows, therefore, that any rate of addition policy which satisfies equation (5.18) will trace out a singular segment satisfying equation (5.22) provided the initial point for such an addition policy also satisfies equation (5.22). Similarly, for $E_2 = 2E_1$, any policies of temperature and rate of addition which mutually satisfy equation (5.31)/(5.32) will also trace out a valid member of the singular segment family (5.22) provided that the initial point for such policies satisfies

equation (5.22). It follows that all possible control policies of θ and r which satisfy equations (5.31)/(5.32) will satisfy the maximum principle.

The Gradients in Function Space method gives an approximation to the solution trajectory which satisfies the maximum principle, and since there is an infinite number of such solutions, the final profiles obtained will be influenced by the initial profiles. Two such final profiles for different initial profiles are shown in Graphs 5.26 and 5.27, and it is seen that the singular segment controls are completely different.

The values of the objective function are close in these two examples, and, for other searches with the same reaction parameters and different initial profiles, the values of the objective function seem to be similarly close in values. From this it would appear that not only is there an infinite number of solutions satisfying the maximum principle, but that these solutions may also all give the same value of the objective function, which may or may not be the maximum value obtainable. It should be stressed that there is insufficient evidence from calculations, and none from theoretical considerations, for this to be any more than a suspicion.

A situation with $E_2 = 2E_1$ is very unlikely to be of practical interest, and since formal proof of whether there is a unique optimal profile could be very difficult, it is not proposed to consider this situation any further. However, the existence of this example is interesting and the difficulties encountered serve as a reminder that application of Pontryagin's maximum principle is not always straightforward.

R_0 = 1.0000

R_{max} = 1.0000

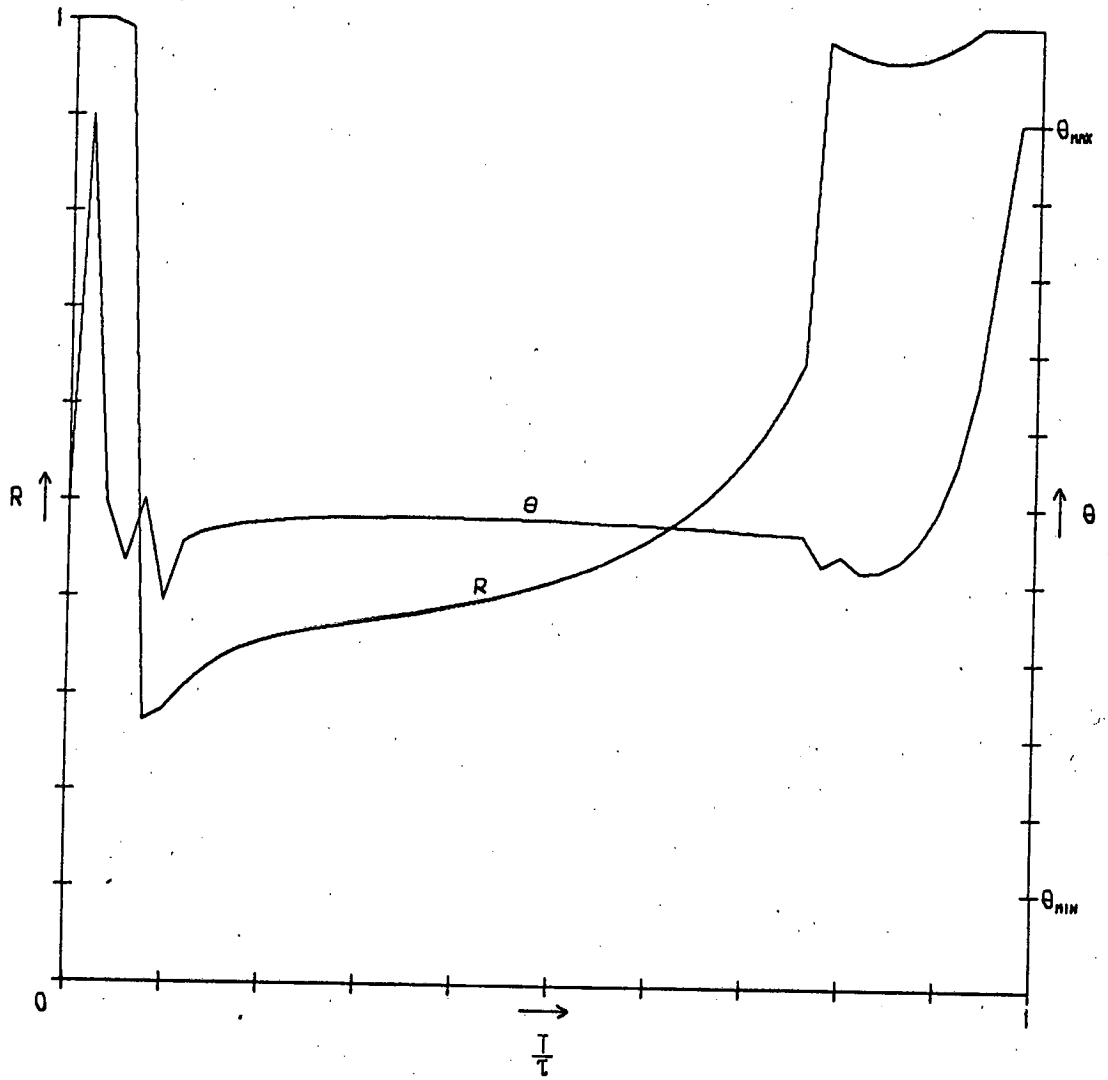
τ = 4.0000

K_1 = 6.1610 x 10^3 EXP(-5000/T)

K_2 = 7.5917 x 10^7 EXP(-10000/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.5729



Graph 5.26

Control policies obtained by the method of Gradients in Function space for $E_2 = 2E_1$. The initial policies were $\theta = 300^{\circ}C$ throughout, and r optimal for this isothermal temperature, as in Graph 3.8 .

A_0 = 1.0000

R_{max} = 1.0000

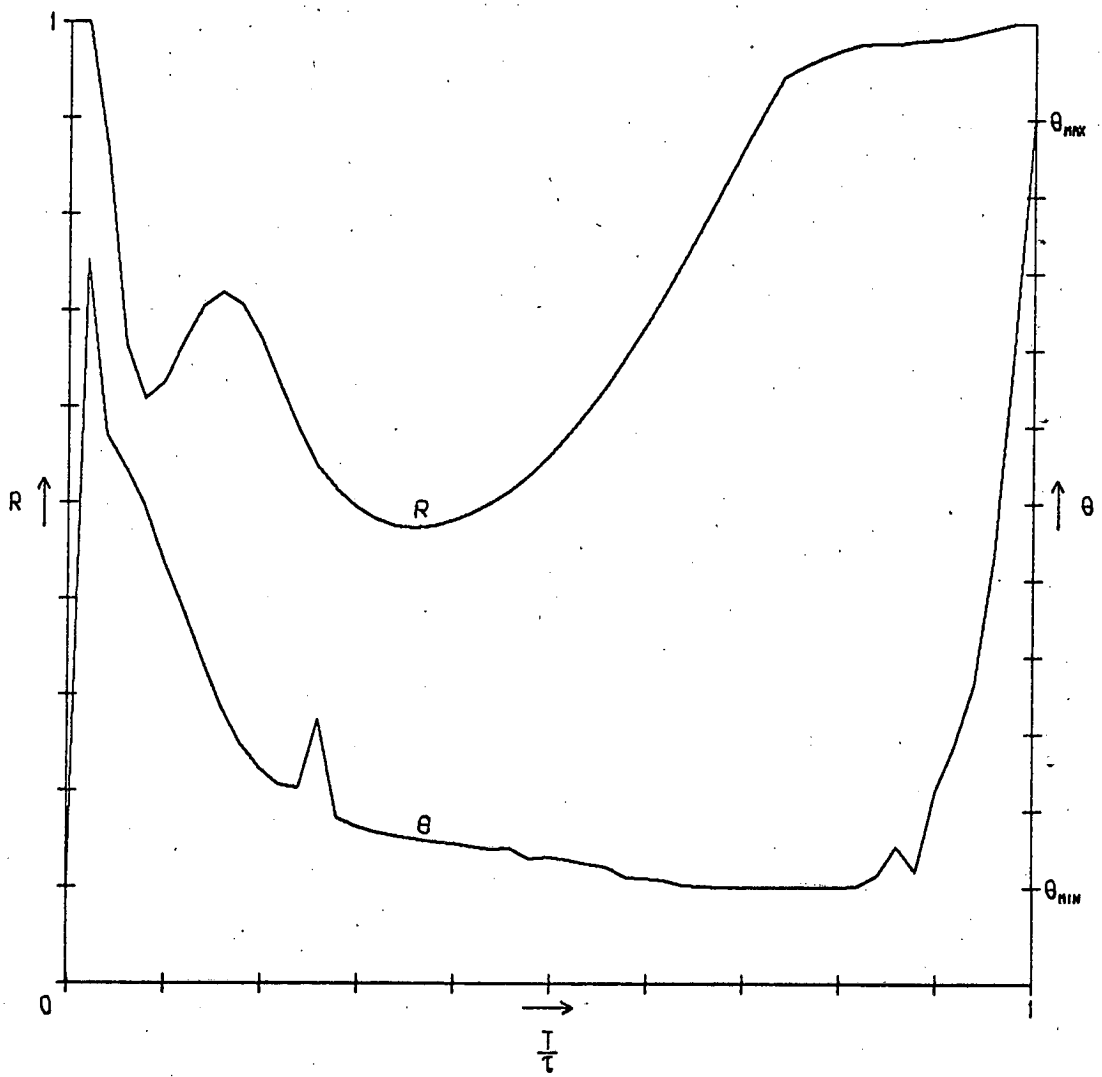
τ = 4.0000

K_1 = 6.1610×10^3 EXP(-5000/T)

K_2 = 7.5917×10^7 EXP(-10000/T)

TEMPERATURE RANGE = 250 TO 350 °C

VALUE OF OBJECTIVE FUNCTION - C(τ) = 0.5728



Graph 5.27

Control policies obtained by the method of Gradients in Function space for $E_2 = 2E_1$. The initial policies were $\theta = \theta_{min}$ throughout and $r = r_{max}$ throughout.

5.3 The Case of $\theta_{min} = 0$

When $E_2 > 2E_1$, the temperature is at its minimum when r takes values between its limits. It is of interest to consider the effect on the optimal control profiles of letting $\theta_{min} = 0$. No reaction will then occur during the singular segment, and it follows, as is shown later, that no singular segment can form part of the optimal trajectory. The investigation is made easier if $r_{max} \to \infty$ and the total amount of B added, Q, is specified. This corresponds to the extensions to the basic isothermal reactor considered in section 4.2 of Chapter 4.

For this situation the state variable and adjoint variable differential equations are as in Chapter 4, which simplify to

$$\frac{da}{dt} = -k_1ab - k_2ab^2; \qquad a(0) = a_o \qquad (5.33)$$

$$\frac{db}{dt} = -k_1ab - 2k_2ab^2 + r; \qquad b(0) = 0 \qquad (5.34)$$

$$\frac{dc}{dt} = k_1ab; \qquad c(0) = 0 \qquad (5.35)$$

$$\frac{dq}{dt} = r; \qquad q(0) = 0; \quad q(\tau) = Q \qquad (5.36)$$

$$\frac{d\lambda_a}{dt} = k_1b(\lambda_a + \lambda_b - 1) + k_2b^2(\lambda_a + 2\lambda_b); \quad \lambda_a(\tau) = 0 \qquad (5.37)$$

$$\frac{d\lambda_b}{dt} = k_1a(\lambda_a + \lambda_b - 1) + 2k_2ab(\lambda_a + 2\lambda_b); \quad \lambda_b(\tau) = 0 \qquad (5.38)$$

$$\frac{d\lambda_c}{dt} = 0 \qquad ; \lambda_c(\tau) = 1 \qquad (5.39)$$

$$\frac{d\mu}{dt} = 0 \qquad ; \quad \mu(\tau) = \gamma \text{ (free)} \qquad (5.40)$$

where γ is free to be chosen in order to obtain the required value of $q(\tau)$.

The Hamiltonian is then

$$H = (\lambda_b + \gamma)r - k_1 ab(\lambda_a + \lambda_b - 1) - k_2 ab^2(\lambda_a + 2\lambda_b) \qquad (5.41)$$

from which

$$\frac{\partial H}{\partial \theta} = \frac{k_1 E_1 ab}{\theta^2}(1 - \lambda_a - \lambda_b) - \frac{k_2 E_2 ab^2}{\theta^2}(\lambda_a + 2\lambda_b) \qquad (5.42)$$

$$\frac{\partial H}{\partial r} = \lambda_b + \gamma \, . \qquad (5.43)$$

For a singular segment, following the arguments in section 4.1 of Chapter 4

$$\lambda_b = -\gamma; \quad \lambda_a = \frac{k_1 + \gamma(k_1 + 4k_2 b)}{k_1 + 2k_2 b} \, . \qquad (5.44)$$

Substitution of these into equation (5.42) gives the value of $\frac{\partial H}{\partial \theta}$ on the singular segment:

$$\left(\frac{\partial H}{\partial \theta}\right)_{\text{singular segment}} = \frac{k_1 k_2 ab^2(1 - \gamma)(2E_1 - E_2)}{\theta^2(k_1 + 2k_2 b)} \, . \qquad (5.45)$$

It has already been shown in Chapter 4 that $\gamma < 1$, and so the sign of $\frac{\partial H}{\partial \theta}$ depends on the relative values of E_2 and E_1, just as before. Thus $\theta = \theta_{max}$ for $E_2 < 2E_1$ or θ_{min} for $E_2 >> 2E_1$ during the singular segment.

For $E_2 < 2E_1$, the optimal temperature control before the modifications of this section were introduced was $\theta = \theta_{max}$ throughout, i.e. isothermal. The system investigated in section 4.2 of Chapter 4, in which the extensions to the rate of addition control are the same as here, was also, by definition, isothermal. By consideration of the isothermal temperature control of the trajectories shown in Graphs 4.26 to 4.28 for

Q = 2.5 and 4.36 to 4.38 for Q = 1.2, it should be possible to ascertain whether isothermal control at maximum temperature is again optimal for these extensions to the rate of addition control.

Let $k_1 = 1$ and $k_2 = 2$ at $\theta = \theta_{max}$. The trajectories of Graphs 4.26 to 4.28 and 4.36 to 4.38 then represent trajectories for $\theta = \theta_{max}$ throughout, and, if this temperature policy is optimal, $\frac{\partial H}{\partial \theta}$ will be positive at all points on these trajectories. It has already been seen that, for $E_2 < 2E_1$, equation (5.45) gives a positive value for $\frac{\partial H}{\partial \theta}$, and so $\theta = \theta_{max}$ on the singular segment. During the final coasting segment λ_a and λ_b are both positive and monotonic decreasing functions for both examples (Graphs 4.28 and 4.38), and it is seen that $\frac{\partial H}{\partial \theta}$ by equation (5.42) then remains positive. $\theta = \theta_{max}$ therefore satisfies the maximum principle during this coasting segment also, and the temperature control for the full solution trajectory becomes $\theta = \theta_{max}$ throughout.

These deductions apply, of course, only to the two particular sets of reaction parameters of the examples in Chapter 4. However, provided that, for other sets of reaction parameters, λ_a and λ_b are both monotone decreasing during the final coasting segment, this temperature control policy will extend to these other cases.

Now suppose that $E_2 > 2E_1$. Then $\frac{\partial H}{\partial \theta} < 0$ on the singular segment and the optimal temperature policy is no longer $\theta = \theta_{max}$ throughout; but it has been stated that $\theta_{min} = 0$, and so a singular segment, where r takes finite values, can form part of the solution trajectory only if $\theta = 0$ everywhere on it. Such a situation corresponds to ceasing the reactions completely for a finite time interval while a quantity of B is added at a finite rate, and is simply a means of consuming batch time

without forming any product. It is obvious that such an interval cannot form part of the optimal policy since an increase in the amount of product formed can be obtained by adding this quantity of B instantaneously at the same point on the reaction path, and using the batch time thus saved for further reaction.

Therefore the optimal control policy can include no finite interval for which r is finite; in addition the total durations for which $r = r_{max}$ must be zero since $r_{max} = \infty$ and the amount of B to be added is specified and finite. It seems, therefore, that B is added instantaneously in discrete amounts at a finite number of points during the reaction. One of these points must obviously be at $t = 0$ (otherwise the reaction cannot start at $t = 0$), but additions of B at later points may also satisfy the maximum principle.

From previous considerations of maximising the Hamiltonian, such instantaneous additions of B can occur only when λ_b approaches $-\gamma$ (a positive quantity) from below, and must cause a change in sign of $\frac{d\lambda_b}{dt}$ if λ_b is to subsequently become less than $-\gamma$. (If λ_b becomes greater than $-\gamma$, the rate of addition becomes $r_{max} = \infty$ for a finite interval, which violates the specification of Q). Instantaneous addition of B causes a discontinuous change in the value of $\frac{d\lambda_b}{dt}$ in equation (5.38), and it is readily shown that this discontinuity does not also cause a change in sign.

For a change in sign of $\frac{d\lambda_b}{dt}$ from positive to negative for a step increase in b (as required for optimality of instantaneous addition of B) it is seen from equation (5.38) that we must have

$$\lambda_a + 2\lambda_b < 0; \tag{5.46}$$

but at this addition of B, $\lambda_b = -\gamma > 0$ (since $\gamma < 0$) and so equation (5.46) can be reduced to

$$\lambda_a + \lambda_b < 0. \tag{5.47}$$

Now if the inequalities (5.46) and (5.47) are substituted into equation (5.38), we obtain

$$\frac{d\lambda_b}{dt} < 0 \tag{5.48}$$

irrespective of the value of b. This contradicts the assumption that $\frac{d\lambda_b}{dt}$ is positive before the addition of B and negative afterwards, and so additions of quantities of B at other than $t = 0$ cannot form part of the optimal policy.

It seems, therefore, that for $E_2 < 2E_1$, the optimal control for the situations of Q specified and r unconstrained corresponding to those examined in Chapter 4 is again $\theta = \theta_{max}$ throughout, as for $E_2 < 2E_1$ in the basic model of the reactor with temperature control. If, for $E_2 > 2E_1$, θ_{min} is additionally allowed to become zero, the optimal addition rate control disappears and is replaced by an instantaneous addition of a quantity Q of B at the beginning of the reaction. The performance of the reactor is then regulated by temperature control alone.

5.4 Discussion

The addition of even an idealised temperature control to the reactor makes the system sufficiently complicated that it is difficult

to make many conclusive deductions about the solution to the maximum principle, and it is necessary in this case to resort to indications from Gradients in Function Space searches. The approximations in the solution trajectory which arise from this method have already been mentioned, and in particular in Graphs 5.9 and 5.13 for $E_2 = 2.1E_1$ and $E_2 = 3E_1$ respectively it is difficult to conclude whether the temperature changes towards the beginning and end of the batch time are smooth and continuous or instantaneous step changes, in the same way as it is not possible to identify the form of the changes in the rate of addition at the beginning and end of the singular segment. In these examples it is possible to prove that instantaneous changes in temperature do not satisfy Pontryagin's conditions, but in a more complicated system such confirmation may not be possible. It has been pointed out in Chapter 2 that blind numerical attack on the solution to the maximum principle is unlikely to be successful, and similarly in this example, incomplete knowledge of the form of the section of temperature control where θ is between its limits would have caused at least considerable difficulty in obtaining an exact solution, if not complete failure. With more complicated extensions to the controls, or less idealised models of the reactor and control system, such algebraic difficulties would be likely to reduce further the features of the control satisfying the maximum principle which can be deduced, and exact solutions would then probably be unobtainable.

In such situations indications from the Gradients in Function Space solutions must be used. The difficulties of interpreting the profiles obtained have already been mentioned, and it has been found in examples in which

$E_2 > 2E_1$ ~~that~~, when the two control variables both have non-trivial optimal profiles, that there is an additional problem of slow convergence, both on the shapes of the profiles and on the value of the objective function. The problem of convergence on the shapes of the control profiles was mentioned in Chapter 3, where it was noted that by taking account of second order variations in deducing the correction functions, algorithms could be obtained which gave better convergence {38 - 42}. However, these are liable to numerical instability if a poor initial approximation to the final profile is used, and for intial searches the starting profile is of necessity a poor approximation. The method suggested by Lapidus and Luus {43}, in which the initial profile for a second order search is obtained by a first order algorithm, would probably work with the example of $E_2 = 3E_1$, but for $E_2 = 2.1E_1$ the convergence with the first order method is so poor (Graphs 5.9 and 5.12) that even this sequential use of first and second order searches might fail.

The Gradients in Function Space method of solution is not ideally suited to all forms of problem. For example, in the first modification to the isothermal system in Chapter 4, where the total amount of B to be added is specified, the value γ of $\mu(\tau)$ is unknown. In a Gradients in Function Space search, calculations of profiles with a guessed value of γ would have to be made (in a similar manner to the search when Q is unspecified in Chapter 3), and then γ adjusted to obtain the desired value of Q. This would involve considerable computation. Further difficulties arise with the second modification to the reactor in Chapter 4, where r is unconstrained. The infinite addition

rate of B for zero time, to give the correct initial concentration of B for the singular segment, would give rise to numerical difficulties.

In addition to these algebraic and computational difficulties, the problems of multiple solutions mentioned by Coward and Jackson {9} may also arise. A situation of E_2 exactly equal to $2E_1$ is most unlikely to occur in practice, but the existence of the multiple solutions to the maximum principle for this case serves as a reminder that this difficulty can be present. In Coward's and Jackson's {9} examples, it was possible to interpret and eliminate many of the non-optimal results, but, as they pointed out, this may not be possible in more complicated examples. Further investigation of the particular case of $E_2 = 2E_1$ with a view to identification and interpretation of non-optimal solution profiles may indeed be very difficult.

For the simple system of r constrained and Q specified it appears that the optimal temperature control for $E_2 < 2E_1$ is the trivial $\theta = \theta_{max}$ throughout, and the extension of the system to r unconstrained and Q specified indicates that this form of control possibly extends to other modifications of the reactor. For $E_2 > 2E_1$ the temperature is $\theta = \theta_{min}$ for the duration of the singular segment and for periods beyond each end of the singular segment. It is seen from Graphs 5.20 and 5.23 that, for $E_2 = 2.1E_1$ and $E_2 = 3E_1$ respectively, the temperature is at θ_{min} for more than 70% of the batch time in each case, and it is therefore of interest to compare the final concentrations of C for the examples of $E_2 = 2.1E_1$ and $E_2 = 3E_1$ for the control satisfying the maximum principle for θ and r and for $\theta = \theta_{min}$ throughout with the r- profile satisfying the maximum principle. It is also informative to compare the values of

Table 5.2

Comparison of values of the objective function for different relative values of E_1 and E_2 for different forms of temperature control. $a_o = 1$, $E_1 = 5000$, $\theta_{min} = 250^oC$, $\theta_{max} = 350^oC$, $r_{max} = 1$, $k_1 = 1$ and $k_2 = 2$ at 300^oC, batch time $\tau = 4$.

$\frac{E_2}{E_1}$	Form of temperature control	$c(\tau)$
-	isothermal at 300^oC (Chapter 3)	0.569
0.9	$\theta = \theta_{max}$ throughout	0.689
1.5	$\theta = \theta_{max}$ throughout	0.626
2.1	solution to maximum principle	0.585
3.0	solution to maximum principle	0.689
2.1	$\theta = \theta_{min}$ throughout	0.575
3.0	$\theta = \theta_{min}$ throughout	0.685

the objective function for the isothermal control of Chapter 3 and for optimal temperature control, the rate of addition profile being optimal for each. The trajectory of Graphs 3.8 to 3.10 is equivalent to isothermal control at 300^oC for a reactor system corresponding to that used for the calculations in this chapter.

The comparisons are given in Table 5.2, where it is seen that the further $\frac{E_2}{E_1}$ is from the value 2, the greater is the improvement in reactor performance. It is also seen that, for $E_2 > 2E_1$, there is only a small decrease in performance when $\theta = \theta_{min}$ throughout the reaction.

A temperature control of $\theta = \theta_{min}$ throughout would therefore be used in a practical environment for these examples, as it is considerably easier to arrange.

By considering $\theta_{min} \to 0$ it is seen intuitively that the decrease in performance by letting $\theta = \theta_{min}$ throughout instead of following the profile which satisfies the maximum principle will not always be small, and in the limit of $\theta_{min} = 0$ the singular segment will disappear, for reasons similar to those given in considering the modification to the reactor of section 5.3 of this chapter. The optimal temperature profile would still have a section of $\theta = \theta_{max}$ at the end of the batch time, and would have $\theta \leq \theta_{max}$ during the earlier stages. Some searches for decreasing values of θ_{min} could give some further insight into the optimal temperature control for $\theta_{min} = 0$.

The investigations in this chapter are intended only as an initial exploration into simultaneous control of temperature and addition of reactant. This exploration has indicated that there are further improvements to be gained for the reaction system considered by adding temperature control to the previously investigated isothermal reactor with distributed addition of reactant, but that the algebra is somewhat more involved, even for the idealised system considered. Exact solutions for more realistic systems may not be possible for this reason, and an approximate solution from the Gradients in Function Space method may be all that can be obtained.

CHAPTER 6

CONCLUSIONS

Although several optimal profiles have been found for a number of different problems associated with the one reaction scheme, and the values of the objective functions have been compared between these different problems, few comparisons with the non-optimal simultaneous initial addition of reactants have been made. Such comparisons are necessary in order to demonstrate the advantage of optimal control. Comparison with the semi-batch reactor, in which all of reactant A is added at the beginning of the batch and the quantity Q of B has its addition distributed uniformly throughout the batch time, should also be made, as it is known [18] that this simple form of distributed reactant addition may give significant improvements in reactor performance when there are competitive reactions.

For simultaneous initial addition with the system of reactions used in this work, there is a value of the initial concentration of B($\equiv$ Q) for a given initial concentration of A which maximises the value of $c(\tau)$. Calculations have shown that this occurs at a value of Q of 1.369, when the value of $c(\tau)$ is 0.3857. The value of $c(\tau)$ for the original optimal rate of addition problem with no constraint on r (Chapter 3) is 0.5760, which is an improvement of nearly 50% over simultaneous initial addition. Even when r_{max} is set at 1.0, the improvement is still better than 47%.

These situations, however, are a little special in that, in

Table 6.1

Comparison of final concentrations of C for isothermal reactors with different control policies. $a_o = 1$, $k_1 = 1$, $k_2 = 2$, $r_{max} = 1$, batch time $\tau = 4$, and total amount of B added, Q, varied.

Q	c(τ) for simultaneous initial addition	c(τ) for uniformly distributed addition	% improvement	c(τ) for optimal control	% improvement
1.2	0.3811	0.4846	27	0.5155	35
1.5	0.3829	0.5287	38	0.5474	43
2.0	0.3255	0.5591	72	0.5656	74
2.5	0.2475	0.5529	123	0.5684	129
2.7	0.2235	0.5456	144	0.5653	153

each case, the value of Q is not previously specified. When this specification is enforced, improvements for large values of Q are somewhat greater, as is shown in Table 6.1. This is simply because, for these large values of Q, the relative quantities of A and B used in the reactions are somewhat different from their stoichiometric ratio for the desired reaction, and the reaction to waste becomes highly favoured in the conditions of high concentration of B which occur at the beginning of the batch after simultaneous addition of reactants. With values of a_o and Q more nearly equal, the improvement is much smaller, and becomes markedly less than the 50% found for comparisons of situations of no specification of Q.

It was noted by Messikommer {21} that for distributed feed plug-

flow tubular reactors with a finite number of sidestream feed points, in which there is a scheme of parallel competitive reactions, a feed of equal fractions of the distributed reactant to each feed point results in only a small decrease in yield compared with the reactor with optimal feed distribution. It is of interest to similarly compare the final concentrations of C for an analogous semi-batch reactor with a constant rate of addition of B, the total quantity, Q, of B added to the reactor being the same as for the optimal policy. This comparison is also shown in Table 6.1, and it is seen that the decrease in performance of a reactor with constant distributed addition of feed is only a few percent less than the reactor with optimal rate of addition and $r_{max} = 1$.

Similar comparison of reactors with and without temperature control cannot be made because insufficient investigations have been made into optimal temperature control. However, from the comparisons made in Table 5.2 it appears that, for $E_2 > 2E_1$, and for the temperature range considered, the simple isothermal control at θ_{min} gives only a very small reduction in performance.

It appears, therefore, that simple non-optimal controls can be found for the reaction scheme studied which give only small decreases in performance compared with the optimal controls. However, this conclusion could not have been reached without evaluation of the optimal control profiles. The improvements of the optimal policies over these simple controls are sufficiently small, particularly for temperature control, that the cost of implementing the optimal control in a practical situation would almost certainly more than absorb the increased profits

accruing from its implementation. This was also the conclusion of Hawkins {22} in his similar study of organic gas/liquid chlorination reactions.

There are many extensions which could be made to the simple idealised model described in this work. For example, problems using conversion of one or other of the reactants, or selectivity of the desired product, as objective functions could be formulated for the same reaction scheme. A great variety of different reaction schemes, both theoretical and real, could also be found which do not satisfy the criterion given in Chapter 2 for optimal simultaneous initial addition. But probably of more value would be to form a more realistic model for the reactor.

As this work has been a preliminary investigation into optimal distributed addition control, the reactor model has been of necessity simple and idealised. The results from such an idealised model would be of little direct value in a practical environment, although the demonstration of the improvement in performance and of the form of the control required for this improvement would be of interest. The dilution effect of adding fresh reactant to the reaction mixture, which was neglected for algebraic convenience, could be included in the model with little difficulty, and would merely have the effect of slightly complicating the algebra without in principle altering the arguments in finding the optimal trajectory. Such a model would then be adequate to describe semi-batch reactions in solution, such as that studied by Hawkins {22}, where the reactions are relatively slow (and the mixing effects are therefore unimportant), and where the temperature effects

are small. For reactions with temperature effect, inclusion of this in the model would again in principle only increase the algebraic complexity. The temperature control described in Chapter 5 could also be made more realistic by substituting for the direct temperature control indirect control, such as heat flux through heating/cooling coils.

Although in principle the arguments would remain the same after incorporation of such modifications, the algebraic complexity could possibly be such as to make some of the derivations from the Maximum Principle very difficult, and an exact solution may then not be obtained. In this situation the Gradients in Function Space method would have to be used, and only an approximation to the optimal control could be obtained. However, an approximation to the optimal control would often be sufficient in practice, since it is unlikely that an exact optimal control could be followed more than approximately in a practical implementation.

Many of the reactions of industrial importance are carried out not in batch reactors but in various forms of tubular reactors, in which it is not possible to incorporate continuous cross-flow feed. Distributed feed of reactant would therefore be limited to a small number of sidestreams, as in Messikommer's {21} investigations, and the continuous model would be used as an upper limit of performance for comparison of reactors with different numbers of feed points. This comparison could then be an aid in deciding on the number of sidestreams.

In practical situations, when the reactor model investigated is idealised and used as an upper limit of performance, the form of the optimal control will often be of secondary importance to the value of the objective function. It has been seen in Chapter 3 that the Gradients

in Function Space method generally converges well on the optimal value of the objective function, although not so well on the control profile, and even in Chapter 5, where there are two control variables, convergence is obtained to within 1% of the optimal value of the objective function. The amount of theoretical derivation required for implementation of this method is minimal, and the Gradients in Function Space method is ideally suited for evaluation of an objective function which is to be used as a limit of performance.

In Chapter 2, when Pontryagin's maximum principle was introduced it was stated that a secondary object of this work was to show how the maximum principle could be used in chemical engineering problems, and some of the difficulties of its use have been demonstrated. The problem of multiple solutions to the maximum principle demonstrated by Coward and Jackson {9} occurred in only one special circumstance in investigations of simultaneous optimisation of rate of addition and temperature controls. However, it has become quite clear during the derivations of optimal profiles that the computational difficulties experienced by other writers {8, 31, 32} with boundary value iteration methods of solution would almost certainly occur in the problems discussed because of the presence of the singular segment. The possibility of singular control is normally easily recognised from the form of the Hamiltonian, and it appears {14, 15, 30, 47} that singular control is not uncommon in chemical engineering optimisation problems. When singularity of the Hamiltonian can occur, it is necessary to attempt to make some algebraic deductions of the form of the control which satisfies Pontryagin's condition in order to obtain an exact control profile, and it has been seen that in all but simple problems

such deductions may not be easy. For example, in Chapter 5 it was not possible to deduce all the features of the solution control, and even in Chapter 3 verification by calculation of the form of the optimal control was required.

Many of the difficulties in these situations of algebraic breakdown can be overcome by the Gradients in Function Space method. For the simple first order algorithm given in Chapter 3 this method normally presents no computational difficulties, and usually converges well on the value of the objective function. It has the disadvantage of poor convergence on the shape of the control profile and, as has been seen, can both disguise features such as discontinuities in the exact optimal profile, and introduce extra features such as oscillations which are not present in the exact profile. Some of these difficulties can be overcome through the better convergence of second order algorithms {38 - 42}, as mentioned in Chapter 3, but the numerical stability of the calculation procedure is jeopardised. It is not known what effect the presence of the singular segment and its associated discontinuities in the control profile for the optimisation problems investigated in this work would have on the convergence and stability of these second order Gradients in Function Space methods; some further investigations could usefully be made into this difficulty.

The Gradients in Function Space method has the additional advantage that, by starting with different initial profiles, some confidence can be gained that a true optimal and not a sub-optimal profile has been obtained. This can often overcome the difficulties of multiple solution mentioned by Coward and Jackson {9}, although, as was seen in

Chapter 5, not always.

It was pointed out in Chapter 5, however, that this method is not ideally suited to all problems to which Pontryagin's maximum principle may be applied. When Q is specified in the problem of optimal reactant addition to an isothermal reactor, for example, the adjoint variable μ corresponding to q has no specified boundary value, and it was shown that an iteration procedure on this boundary value, with a complete calculation of the control profile for each adjustment, would be required to obtain the desired value of Q. The computational load would therefore be very great. Removing the limit on the maximum rate of addition of reactant would also cause computational difficulties if instantaneous addition of a quantity of reactant was required as part of the optimal control. Such instantaneous addition would be approximated by a very large rate of addition for a short time in a Gradients in Function Space solution, which would be liable to cause numerical difficulties.

In conclusion, therefore, it is seen that, for the reactions and reactor systems considered, optimal distributed addition profiles for reactant B can be found which give distinct improvements in reactor performance over simultaneous initial addition, but that improvements of only slightly less magnitude can be obtained by a simple non-optimal policy of uniform distribution throughout the reaction trajectory. When the temperature of the reaction mixture is simultaneously optimised, further improvements in performance are obtained, the optimal temperature control being isothermal at θ_{max} for $E_2 < 2E_1$, and non-isothermal for $E_2 > 2E_1$. However, again simple non-optimal isothermal control at

$\theta = \theta_{min}$ for $E_2 > 2E_1$ gives only a very small reduction in the value of the objective function. The application of Pontryagin's maximum principle is well suited to the problems investigated, but algebraic deductions from Pontryagin's condition are required before an exact control profile can be obtained. For many practical purposes, particularly if the value of the objective function is of greater importance than the exact form of control, the method of Gradients in Function Space is probably more useful, as it is usually much simpler to apply.

APPENDIX I

DEMONSTRATION OF DIFFERENCES IN SINGULAR SEGMENTS FOR DIFFERENT VALUES OF Q AND THE SAME VALUES OF τ

The calculations of solution trajectories referred to in this Appendix are those of Section 4.1.2 of Chapter 4.

From equation (4.13) for the singular segment in the a - b plane a value of a can be extracted

$$a = \frac{(k_1 N + \gamma r_{max} \text{ sgn } 1(\gamma))(k_1 + 2k_2 b)}{k_1 k_2 b^2 (1 - \gamma)} .$$

If this is substituted into equation (4.12) for the rate of addition of B on the singular segment, a is eliminated

$$r = \frac{(k_1 + 2k_2 b)^2}{k_1 k_2 b (1 - \gamma)} \left(\frac{k_1 k_2 b^3 (1 - \gamma)}{2(k_1 + 2k_2 b)} + k_1 N + \gamma r_{max} \text{ sgn } 1(\gamma) \right)$$

which is not independent of γ. From the calculations summarised in Table 4.1, the values of γ for Q = 1.5, 2.0 and 2.5 are approximately - 0.071, - 0.015 and + 0.006 respectively, and such values of γ will give values of r for a given value of b which differ by only small amounts, assuming that N is constant.

The value of N, however, also varies for calculations of trajectories with different values of Q if the batch time is to remain the same, but this variation in N is not sufficient to compensate the corresponding variation in γ. Taking a value of b of 0.3, say (this is approximately in the middle of the singular segment for each value of

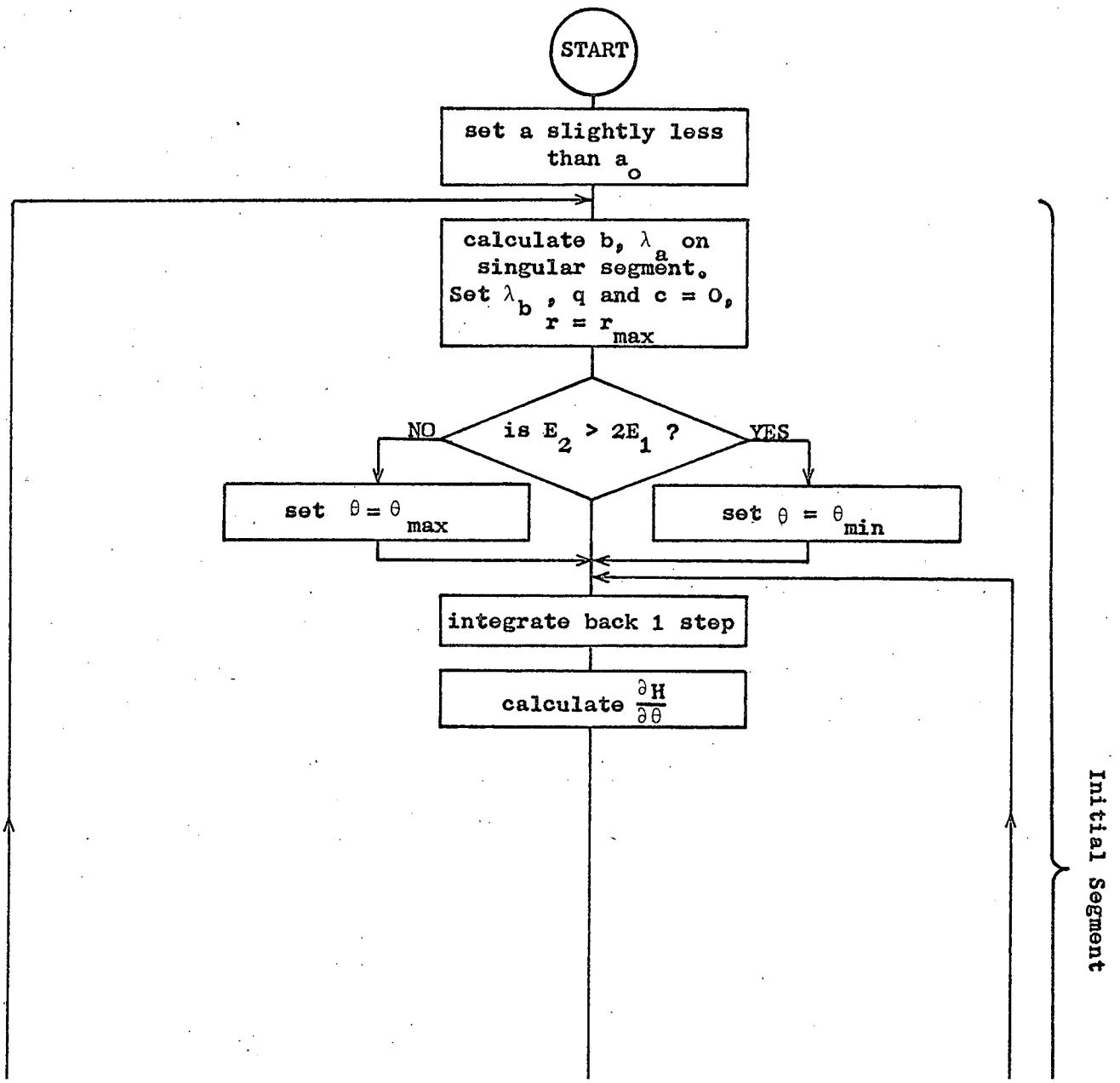
Q in these trajectories), and substituting exact values from Table 4.1 for N and γ, values of r of 0.4323, 0.4331 and 0.4392 are obtained for Q = 1.5, 2.0 and 2.5 respectively.

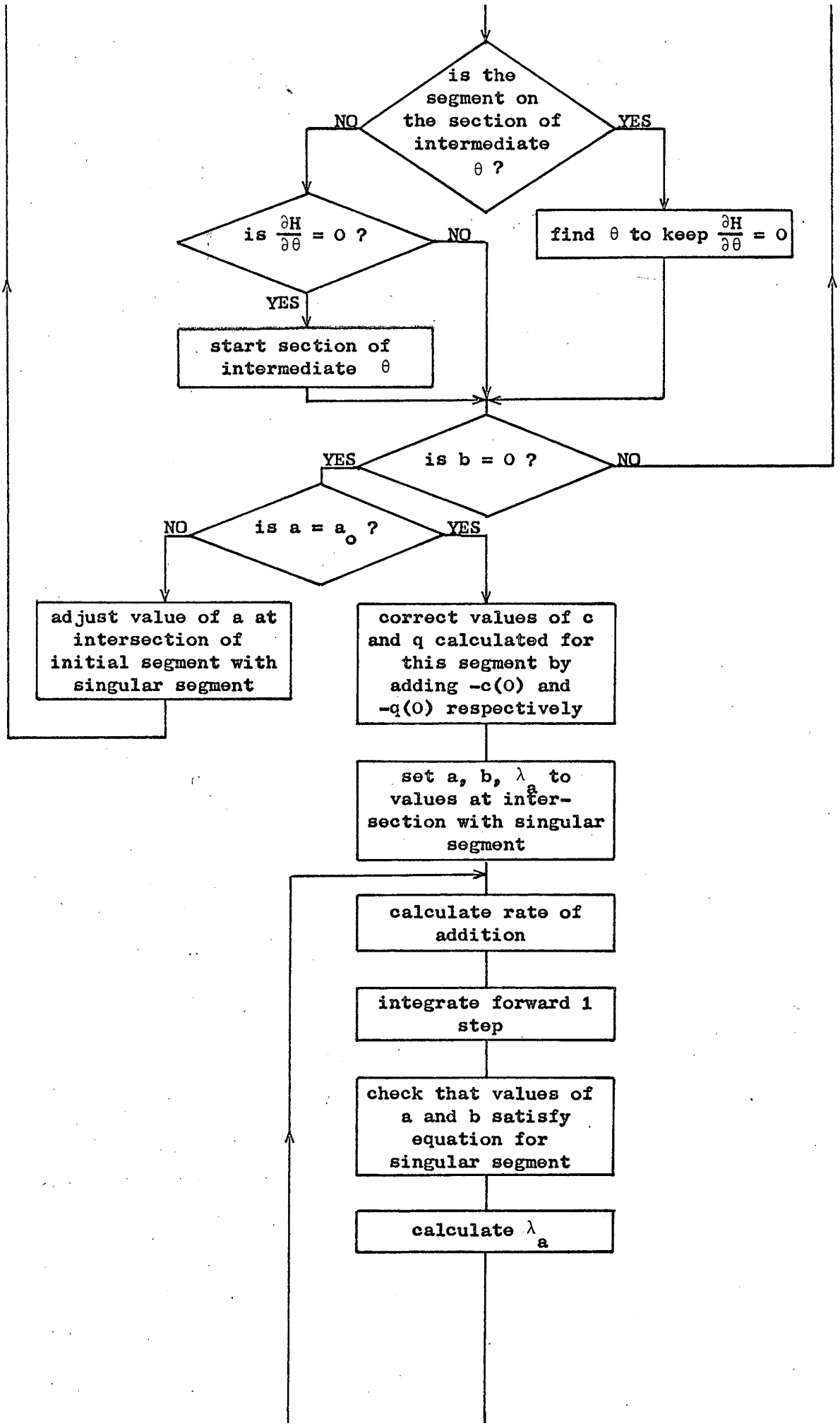
Therefore, although the control policies for the singular segments are very similar, they are distinct.

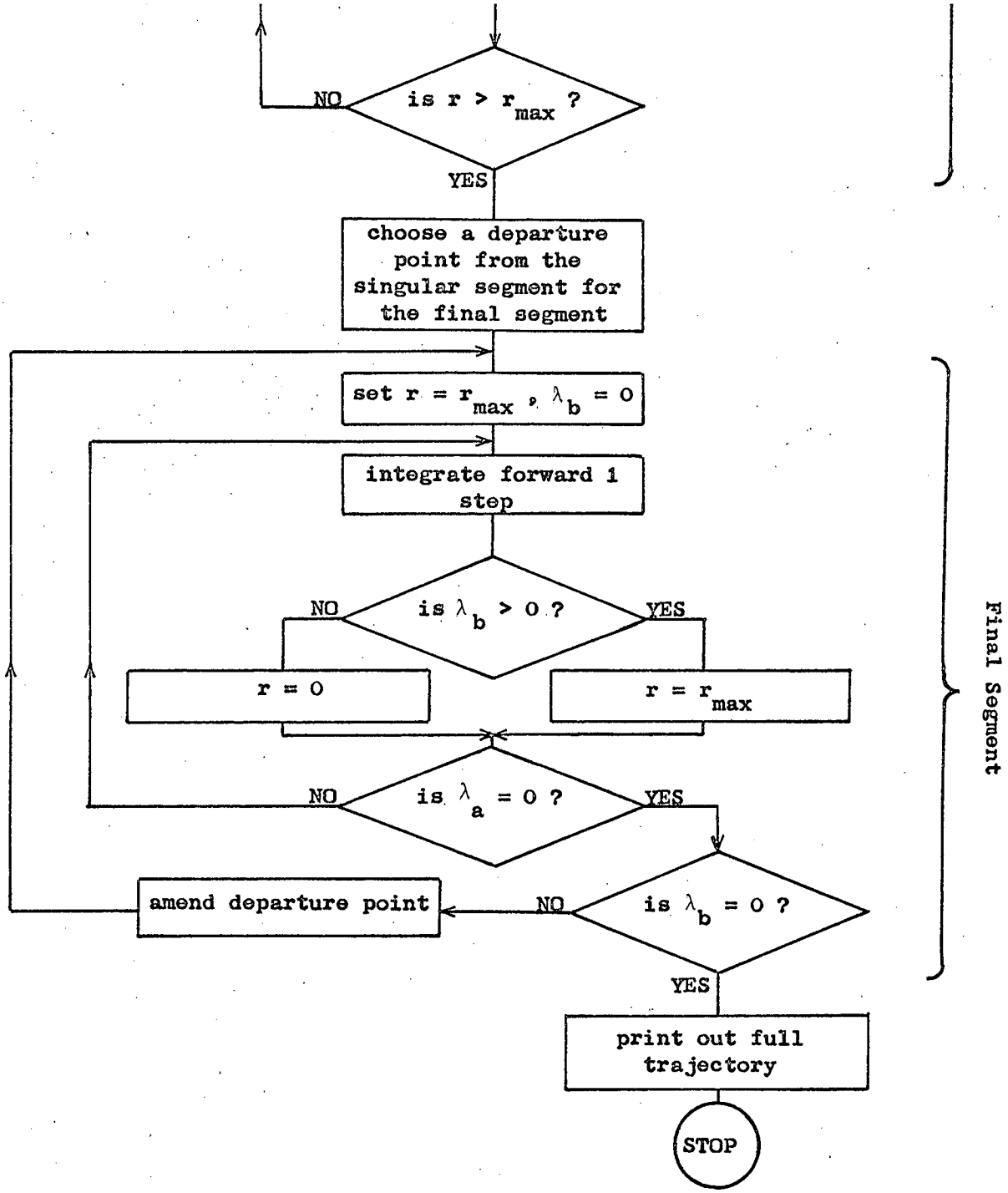
APPENDIX II.

FLOW DIAGRAM OF CALCULATION PROCEDURE OF EXACT TRAJECTORY FOR SIMULTANEOUS TEMPERATURE CONTROL AND RATE OF ADDITION CONTROL.

This flow diagram summarises the important features of the detailed calculation procedure used to evaluate the exact profiles described in section 5.1 of Chapter 5. In particular, the details of adjusting the step lengths to avoid overstepping such points as those where $\frac{\partial H}{\partial \theta}$ reaches zero and where b reaches zero in the first segment have been omitted.




is the segment on the section of intermediate θ ?
NO
YES
is $\frac{\partial H}{\partial \theta} = 0$?
NO
YES
find θ to keep $\frac{\partial H}{\partial \theta} = 0$
start section of intermediate θ
is b = 0 ?
YES
NO
is a = a_o ?
NO
YES
adjust value of a at intersection of initial segment with singular segment
correct values of c and q calculated for this segment by adding -c(0) and -q(0) respectively
set a, b, λ_a to values at intersection with singular segment
calculate rate of addition
integrate forward 1 step
check that values of a and b satisfy equation for singular segment
calculate λ_a
Initial Segment
Singular Segment



This calculation of the trajectory gives a value of batch time which is dependent on the value of N given. To obtain a desired batch time, this value of N must be adjusted and the whole calculation procedure above repeated.

NOMENCLATURE

A	chemical component
a, a(t)	concentration of A
a_o	initial concentration of A, a(0)
B	chemical component
b, b(t)	concentration of B
C	chemical component
c, c(t)	concentration of C
c_i, $c_i(t)$	number of moles of chemical components
D	chemical component
E, F	chemical components
E_1, E_2	activation energies of reactions divided by the Universal Gas Constant
f_i	derivatives of state variables x_i
H	Hamiltonian function
H_{max}	maximum value of H
H_τ	value of H at $t = \tau$
I	set of indices denoting reactants
k_1, k_2, k_3	kinetic constants of reactions
N	$= a(\tau)b(\tau)$
P	objective function to be maximised or minimised
Q	total amount of component B added during batch time
q, q(t)	amount of B added since beginning of reaction
Q_i	total amount of i'th reactant added during batch time
q_i, $q_i(t)$	amount of i'th reactant added since beginning of reaction
r, r(t)	rate of addition of component B

r_{max}	maximum value of r
$r_i, r_i(t)$	rate of addition of i'th component
$r_{i\ max}$	maximum value of r_i
sgn $1(\gamma)$	modified signum function, defined by equation (4.6)
t	time since beginning of reaction
$u, u(t)$	single control variable
u_{min}	minimum value of u
u_{max}	maximum value of u
$u_i, u_i(t)$	control variables
$x_i, x_i(t)$	state variables
x_i^o	initial value of x_i
x_i^f	specified value of x_i at $t = \tau$
z	constant of integration
α_i	constants defining the objective function
α, β, γ	constants; in particular, γ is taken as the value of $\mu(\tau)$ in Chapters 4 and 5
$\delta q, \delta q(t)$	quantity of B added instantaneously to reaction mixture
$\delta r, \delta r(t)$	correction function on r for Gradients in Function Space method
$\delta u, \delta u(t)$	correction function on u for Gradients in Function Space method
$\delta\theta, \delta\theta(t)$	correction function on θ for Gradients in Function Space method
$\epsilon, \epsilon_1, \epsilon_2$	positive correction parameters for Gradients in Function Space method
η_1, η_2	adjoint variables corresponding to ξ_1, ξ_2
$\lambda_i, \lambda_i(t)$	adjoint variables corresponding to the c_i

$\theta, \theta(t)$	temperature of reaction mixture
θ_{max}	maximum permitted value of θ
θ_{min}	minimum permitted value of θ
μ	adjoint variable corresponding to q
$\mu_i, \mu_i(t)$	adjoint variables corresponding to the q_i
ν_i^r	stoichiometric coefficients in the r'th reaction
ξ_1, ξ_2	extents of reactions
$\rho^r(c)$	rate of r'th reaction as a function of the c_i's
τ	total batch time

Most of the graphs of solution trajectories in this thesis were plotted on an incremental graph plotter driven by a digital computer. The character set available with this plotter is limited to capital letters, and so there are some discrepancies between the nomenclature on these graphs and the nomenclature in the text. The symbols A, B, C and R in these graphs therefore stand for a, b, c and r respectively in the text.

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